

PCT INTERNATIONAL COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents
 United States Patent and Trademark
 Office
 Box PCT
 Washington, D.C. 20231
 ÉTATS-UNIS D'AMÉRIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 23 September 1999 (23.09.99)	
International application No. PCT/IL99/00097	Applicant's or agent's file reference 8244
International filing date (day/month/year) 16 February 1999 (16.02.99)	Priority date (day/month/year) 26 February 1998 (26.02.98)
Applicant GARTI, Nissim et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:

06 July 1999 (06.07.99)

☐ in a notice effecting later election filed with the International Bureau on:2. The election ☒ was☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer C. Carrié Telephone No.: (41-22) 338.83.38
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TENT COOPERATION TREAT

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 8244	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/IL 99/ 00097	International filing date (day/month/year) 16/02/1999	(Earliest) Priority Date (day/month/year) 26/02/1998
Applicant YISSUM RESEARCH DEVELOPMENT COMPANY OF THE HEBREW;		
<p>This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.</p> <p>This International Search Report consists of a total of <u>2</u> sheets. <input checked="" type="checkbox"/> It is also accompanied by a copy of each prior art document cited in this report.</p>		
<p>1. Basis of the report</p> <p>a. With regard to the language, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.</p> <p><input type="checkbox"/> the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).</p> <p>b. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international search was carried out on the basis of the sequence listing :</p> <p><input type="checkbox"/> contained in the international application in written form.</p> <p><input type="checkbox"/> filed together with the international application in computer readable form.</p> <p><input type="checkbox"/> furnished subsequently to this Authority in written form.</p> <p><input type="checkbox"/> furnished subsequently to this Authority in computer readable form.</p> <p><input type="checkbox"/> the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.</p> <p><input type="checkbox"/> the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished</p> <p>2. <input type="checkbox"/> Certain claims were found unsearchable (See Box I).</p> <p>3. <input type="checkbox"/> Unity of invention is lacking (see Box II).</p> <p>4. With regard to the title,</p> <p><input checked="" type="checkbox"/> the text is approved as submitted by the applicant.</p> <p><input type="checkbox"/> the text has been established by this Authority to read as follows:</p> <p>5. With regard to the abstract,</p> <p><input checked="" type="checkbox"/> the text is approved as submitted by the applicant.</p> <p><input type="checkbox"/> the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.</p> <p>6. The figure of the drawings to be published with the abstract is Figure No. _____</p> <p><input type="checkbox"/> as suggested by the applicant. <input type="checkbox"/> None of the figures.</p> <p><input type="checkbox"/> because the applicant failed to suggest a figure.</p> <p><input type="checkbox"/> because this figure better characterizes the invention.</p>		

INTERNATIONAL SEARCH REPORT

National Application No.

IL 99/00097

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01J13/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 24224 A (HEATH J.R. ET AL) 10 July 1997 see claims 1-30 -----	1,3,5,7, 8,10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

12 May 1999

Date of mailing of the international search report

21/05/1999

Name and mailing address of the ISA

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Authorized officer

Fouquier, J-P

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

/US 99/02011

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 29708277 U	09-10-1997	NONE	
US 4799678 A	24-01-1989	AU 1128188 A GB 2200564 A	11-08-1988 10-08-1988
US 3733074 A	15-05-1973	NONE	

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 8244	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/IL 99/ 00097	International filing date (day/month/year) 16/02/1999	(Earliest) Priority Date (day/month/year) 26/02/1998
Applicant YISSUM RESEARCH DEVELOPMENT COMPANY OF THE HEBREW;		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 2 sheets.



It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.



the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :



contained in the international application in written form.



filed together with the international application in computer readable form.



furnished subsequently to this Authority in written form.



furnished subsequently to this Authority in computer readable form.



the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.



the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,



the text is approved as submitted by the applicant.



the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,



the text is approved as submitted by the applicant.



the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.



as suggested by the applicant.



because the applicant failed to suggest a figure.



because this figure better characterizes the invention.



None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No.

/IL 99/00097

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B01J13/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 24224 A (HEATH J.R. ET AL) 10 July 1997 see claims 1-30 -----	1,3,5,7, 8,10

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"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

12 May 1999

Date of mailing of the international search report

21/05/1999

Name and mailing address of the ISA

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Authorized officer

Fouquier, J-P

INTERNATIONAL SEARCH REPORT

In on on patent family members

International Application No
/IL 99/00097

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
W0 9724224 A	10-07-1997	AU 1743397 A	28-07-1997
		CA 2241183 A	10-07-1997
		EP 0914244 A	12-05-1999

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 8244	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/IL99/00097	International filing date (day/month/year) 16/02/1999	Priority date (day/month/year) 26/02/1998
International Patent Classification (IPC) or national classification and IPC B01J13/02		
Applicant YISSUM RESEARCH DEVELOPMENT COMPANY OF THE..et al.		


1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 7 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 10 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☒ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 06/07/1999	Date of completion of this report 16.03.2000
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Gosselin, D Telephone No. +49 89 2399 8400



**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/IL99/00097

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-8 as received on 27/02/2000 with letter of 27/02/2000

Claims, No.:

1-11 as received on 27/02/2000 with letter of 27/02/2000

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been examined in respect of:

- ☐ the entire international application.
☒ claims Nos. 2,6.

because:

- ☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (*specify*):

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/IL99/00097

- ☒ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. 2,6 are so unclear that no meaningful opinion could be formed (*specify*):

see separate sheet

- ☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed.
- ☐ no international search report has been established for the said claims Nos. .

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims
	No:	Claims 1,3-5,7,10
Inventive step (IS)	Yes:	Claims
	No:	Claims 8,9,11
Industrial applicability (IA)	Yes:	Claims 1,3-5,7-11
	No:	Claims

2. Citations and explanations

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Re Item I

The text of the description and the claims have completely revised, although the nature of the amendments was identified by reference to the application documents as originally filed, the applicant failed to indicate the support of the various amendments in the application documents as originally filed. Among these amendments, no explicit support could be found for the introduction of "in water-organic-surfactant organized solutions" into line 22 of page 3.

However, the amended claims seems to meet the requirements of Article 34.2)b) and Rule 66.8 PCT. More particularly, the addition of the terms "metal salts" in claim 1 and at the corresponding part in the description, page 4, seems to be supported by the first paragraph of page 1 as originally filed.

Re Item III

Claims 2 and 6 were not considered, because the technical features of these claims does not meet the requirements of Article 6 PCT (Cf. Item VIII).

Re Item V

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Reference is made to the following document:

D1 = WO 97 24 224 A

2. D1 discloses a process for the preparation of nanoparticles of metals. The particles are synthesised from solution of precursors, which are reacted with a reducing agent. The method involves the use of a surfactant. In view of the examples, the reaction conditions can be qualified as mild. The nanoparticles can be additionally dispersed in a polymer solution. The solvent comprises ethers and chlorinated hydrocarbons. The polymers i.a. polymethylmetacrylate. (D1: claims

more particularly claims 1, 14, 20, 21, 23 and 24).

Notwithstanding the objections under Article 6 PCT (Re Item VIII) the method according to claims 1, 3 to 5, 7 and 10 of the application lacks novelty in terms of Article 33(1) and (2) PCT over the content of D1.

3. The subject-matter of claims 8, 9 and 11 is apparently novel in view of D1. These dependent claims do not apparently contain any features which, in combination with the features of any claim to which they refer, could meet the requirements of the PCT in respect of inventive step. Such a combination could only be regarded as inventive, if the technical features of these claims should be responsible for unexpected effects or properties by comparison with the method of claims 1, 3-5, 7 and 10, which is known from D1. However, no such effects or properties are indicated in the application.

Hence, no inventive step is present in the subject-matter of claims 8, 9 and 11.

Re Item VIII

Certain observations on the international application

1. The abusive use of non conventional terms and relative terms renders the subject-matter of the claims as a whole obscure.
 - 1a. In common language, a (metal) precursor would be the starting material, which after reaction, leads to metal, metal oxide or ceramics nanoparticles. All the surfactants do not belong to this type of materials, although according to claim 1, the precursor is a compound selected among surfactants (in general) and alkoxides.

In a letter of reply dated 16.01.2000, the applicant referred to "special surfactants comprising metal ions, which are reduced (for instance, Cu, Cd sulfocinate or $(\text{PdCl}_4)(\text{R}_4\text{N})$ where (RN_4) is a quaternary ammonium cation" as metal precursors. However, these special surfactants are not referred to in the application as originally filed. According to the description, page 5, there do not even belong to

the preferred surfactants. It is finally submitted that the surfactants are not referred to as precursors in the first paragraph of page 1 of the description as originally filed.

Apparently, the terms "surfactants" seems to have been simply used in place of "metal salts" (Cf. claim 9 and page 1, first paragraph).

- 1b. In the present form, the method of claim 1 is merely defined by reference to the technical problem that the applicant intends to solve. Claim 1 does not meet the requirements of Article 6 and Rule 6 PCT in that the matter for which protection is sought is not clearly defined. The technical features "suitable" or necessary for achieving this result should be added.

By the way, the terms "as herein defined" in claim 1 should be replaced by the definition of the nanoparticles (nanomaterials) indicated in the description, page 1, first paragraph.

- 1c. It is also submitted that there is a discrepancy between the subject-matter of claim 1 and the description, page 4, lines 19-28. According to the description, the feature of claim 2 is an essential feature, which is moreover not properly defined.
- 1d. The terms "non freezing water" is not a definition commonly recognised in the art for steady state of water. Since this term is not concisely defined in the application and the publications cited in the application are not available to the examiner, claims 1 and 2 do also not meet the requirement of clarity and conciseness in view of these terms. The article of Senatra (ref.18) was not filed. The applicant did not comment how it is possible to prepare a complex liquids, where the whole water is non freezing water, and did failed to show the form of this non freezing water in the liquid. It is doubtful that a metastable state in which "non freezing water" could be present can be maintained during the method of production of nanoparticles, which necessarily involves shearing action in the dispersion.

In view of the information contained in the description, non freezing water should correspond to water molecules strongly bond to a surface. In the present case, the compounds to the surface of which the water is bounded is not identified.

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/IL99/00097

- 1e. The terms "organized water-organic surfactants" or "organized-water-organic surfactants" is not understood. Microemulsions and liquid crystalline media, which are mentioned by way of example at page 4, penultimate paragraph, does not necessarily comprise an organic surfactant. The structure of such a compound and the nature of the bound with metal particles or water is not understood.

In the context of the application, the meaning of "organized" is also obscure.

It further appears that the wording of claim 6 is not consistent with that of the description, page 4, lines 38-40. Apparently one should read "organized-water-organic surfactant solutions" in claim 6 (letter of reply dated 16.01.2000).

METHODS FOR THE PREPARATION OF NANOSIZED MATERIAL PARTICLES

The present invention relates to the methods for the preparation of nanosized material particles. ("Nano-materials" in connection with the present invention comprise transition metals and alloys; metal oxides; and ceramic compositions having a small nanosize, i.e. about 1 - 6 nm.) Nanomaterials are prepared from the corresponding precursors i.e. the corresponding metal salts or alkoxides by suitable chemical reactions, e.g. reduction, hydrolysis and exchange processes under mild conditions.

There are known methods to prepare clusters or fine colloids from said nanomaterials which are dispersed in different suitable solutions. Appropriate liquid media enable the production of different preparations, which may be used as thin films on various supports.

There are known several methods for the preparation of ultrathin films of metal particles on solid supports, e.g. ion implantation (M.Che. C.O. Bennet, Adv. Catal. 1989, 36, 55); organometallic chemical vapor deposition (A. Sherman, Chemical Vapor Deposition for Microelectronics, Principles, Technology and Application, Noyes Publications; Park Ridge, N.J. 1987; and N.H. Dryden et. al., Chem. Mater. 1991, 3, 677); metal deposition from colloidal solution (G.Schmid, Chem. Rev. 1992, 92, 1709); reductive metal deposition from aqueous salt solution (I.Coulthard, et. al., Langmuir 1993, 9, 3441.); photodecomposition of metal complexes in thin films (R.Krasnasky et. al. Langmuir, 1991, 7, 2881); and photo-reductive deposition from Pd(II) complexes in solution (K. Kondo et. al., Chem. Lett. 1992, 999). Other technics are based on the film formation of noble metal loaded block copolymers (Y.NgCheongChan et. al., Chem.Mater. 1992, 4, 24; and J.P.Spatz, et al., Adv. Mater. 1995, 7, 731.); on the Langmuir-Blodgett (LB) transfer of monolayers or surfactant stabilized metal colloids (F.S. Meldrum et. al., Langmuir 1994, 10, 2035; and F.S. Meldrum et al., Chem. Mater. 1995, 7, 1112); and on thermal decomposition of LB films of zero valent palladium complexes (E.

Maassen et. al., Langmuir 1996, 12, 5601).

At present the microelectronic and some related industries, mainly continue to use the vapor deposition method. The "Wet" method, which is a method of film deposition from solutions, provides a good challenge for the industry since it does not require high temperatures and pressures or high vacuum and enables to vary the properties of the nano compositions to a large extent

During the last decade, the number of scientific works devoted to the synthesis of nanomaterials in solutions has significantly increased. Certain practical results were reported. Thus, for example G. Schmid (see above) demonstrated that the pellets which consist of ligand stabilized golden clusters (derived from a liquid) may be regarded as tunneling resonance resistors and, additionally, as cellular automates. The density of electronic switches, compared with common semiconductors increased in another example to a factor of 10^5 - 10^6 . Another paper (T. Yamamoto, in Macromolecular Complexes, Ed. by Eishun Tsuchida, VCH, 1993, 380-395.) informed about the preparation of electrically conducting polymer compositions by using organosols of metal sulfides. The polymer-composite films not only show good electrical conductivity but were also controlled to p- or n-type conductors.

The realization of quantum dots, of uniform size and structure opens the door to multiple switches. This enables the manufacture of new generations of computers with extremely high capacities. The manufacture of novel mini-lasers, based on quantisizing particles, will most probably lead to optoelectronic switches, operated simultaneously by photons and electrons. Nanometal coatings may be effectively used, e.g. as film catalysts (for instance in the processes of electroless metal deposition); and as modifiers of mechanical properties of different materials.

However, all said conventional methods are not satisfactory in the preparation of coatings comprising nanomaterial particles, as they are rather complicated, expensive or do not yield the particles having the desired size.

It has thus been desirable to find a method which would

overcome said disadvantages, i.e. should not be complicated, not be too expensive and yield nanomaterial particles having the desired size.

It is well known that water which appears to be a key factor which governs the association of surfactants in different solvents, functions not only as an inert solvent but plays a significant part in the mechanism of chemical processes. (Garti et. al. Coll. & Interface Sci. 178 (1996) p. 60-68). When describing the state of water in relation to any surface a distinction is usually made between "bulk" and "bound" water. It is assumed that "bulk" or free water has physico-chemical properties which are not very different from those of pure water. "Bound" water may be defined by the operational definitions which refer to the water detected by a certain technique.

According to the method utilized by Senatra (D. Senatra et. al. Can. J. of Phys. 68 (1990) p. 1041), in which the endothermic scaling mode was applied and the peaks representing various states of water were identified and analyzed, it was shown that "free" water melts at 0°C, "interfacial bound" water melts at -10°C, and non-freezing water which is the most strongly bound part of bound water has no peaks on thermograms up to -100°C.

It has been found that the state of the water in water-organic-surfactant organized solutions is strictly correlated with the size of the particles. Particles which have a diameter of less than 5 nm are synthesized in systems which comprise only strongly bound water (non freezing water according to subzero differential scanning Calorimetry DSC).

In developing the method according to the present invention it has been considered:

- a. producing the water-organic-surfactant organized solutions (complex liquids) comprising nanosized particles in particular having a diameter of 1- 5 nm which are useful for the particle preparation;
- b. regulating the water content in such a manner that the whole water will be strongly bound to the surfactant (non-freezing) in the system, thus enabling to provide nano particles which have a diameter of less than 5 nm;
- c. the regulation of the solution structures which enables

d. the variation of the chemical composition and concentration of nano-precursors (and of the complementary reactants), which enables the control of the particle size distributions (PSD) and of the thickness of the protecting shells;

f. the control of the viscosity and of the velocity of the solutions which lead to different film thicknesses;

The present invention thus consists in a method for the production of nanomaterial particles (as herein defined) in which:

preparing from said materials fine colloids dispersed in various polymer solutions.

The water in the solution is advantageously non-freezing water as determined by low temperature differential scanning calorimetry

Mild conditions in connection with the present invention are suitably atmospheric pressure and a temperature range of room temperature to 70°C.

Suitable organic solvents may be, e.g. selected among

suitable hydrocarbons (octane, decane, dodecane); chlorinated hydrocarbons (1,2 - dichloroethane); ethers (ethylether); etc.

The appropriate liquid media enable the preparation of different self assemblies of nanomaterials and subsequently the use of them as thin films on various supports.

Suitable surfactants are, for example,:

Quaternary ammonium salts, e.g. trioctylmethyl ammonium chloride (aliquat 336), dioctyldimethylammonium bromide (DDAB), cetyltrimethylammonium chloride (CTAB), etc.; sodium bis-(2-ethyl-hexyl)- sulfosuccinate; poly-ethoxyethylene-10-oleyl ether (Brij 96; etc.

Oxide precursors may be, e.g.

alkoxides:

tetraethoxy silane (TEOS); tetramethoxy silane (TMOS); Al, Zr isopropoxides, etc;

Fe, Mg and Al chlorides; Al and Mg acetates; Na and K orthosilicates; Zr oxychloride; etc. Metal precursors may be, e.g. transition metal salts of Fe, Co, Ni, Cu, Ru, Rh, Pd, Ir and Pt, e.g. FeCl_3 , K_2PdCl_4 , K_2PtCl_6 and CuCl_2 .

The polymers may be selected, e.g. from polyethylene oxide (PEO), polyvinyl chloride (PVC), polyvinyl alcohol (PVA), polymethyl methacrylate (PMMA), etc.

Suitable reducing agents are, for example, sodium formate; hydrogen; certain alcohols (methanol, ethanol, isopropylalcohol); etc.

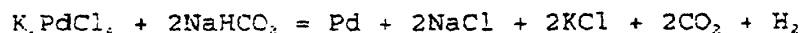
The method according to the present invention can direct the morphology, dimension and homogeneity of the size distributions of the small colloids (and clusters) and also their self assembling.

Example 1

A Pd colloidal dispersion was prepared from a solution containing 12% wt of hydrated trioctylmethylammonium chloride (aliquat 336) which corresponds to water/aliquat molar ratio = 3.06. Sub-zero DSC analysis did not reveal any peak which belongs to interfacial (-10°C) and free water (0°C) in the precursor solution.

Potassium tetrachloropalladate (K_2PdCl_4) (326mg) was solubilized in a 5 ml aliquat-dichloroethane-water mixture. Sodium

formate (NaHCO_3) (0.22 gr) was poured onto the mixture under argon. The reaction was carried out in accordance with the following formula:



The reaction was carried out at 75°C. In the course of the reaction, the orange color gradually changed to a dark brown color. The reaction was stopped after 1 hour and the dichloroethane was evaporated from the reaction mixture. The waxy residue obtained, was washed, in order to remove the inorganic salts, with deionized water and dried at 30 torr and 50°C.

Electron diffraction data revealed a face centered-cubic (fcc) Pd phase, while Transmission Electron Microscopy (TEM) analysis showed round particles having a mean diameter of 1.8 nm.

The nanometal prepared was redispersed in 40 ml of dichloroethane containing 30% of a v/v Polyvinyl alcohol (PVA). The viscosity of the solution was 40 cps.

The surface of a glass plate was thoroughly cleaned with hot water, methyl alcohol and diethyl ether. A coating was prepared by drawing with the velocity of 8 mm/sec. The bright orange transparent film obtained had a magnitude of electrical conductivity $10^{-8} \Omega^{-1}\text{cm}^{-1}$.

Example 2

1.25 g of a commercially available nonionic surfactant Brij-96 (poly-ethoxyethylene-10-oyleyl ether $\text{C}_{18}\text{H}_{35}(\text{OCH}_2\text{CH}_2)_9\text{OH}$ (PEO) was added to a mixture of 4 ml of hexane and 1.18 g of i-butanol. 1 ml of a 0.025M solution of FeCl_3 in 0.01 HCl was then poured on the mixture. The mixture was homogenized by Vortex and it then looked like a homogenous solution. The sub-zero DSC analysis did not reveal any peak which belong to freezing water. After an ageing process at 40°C in the course of 48 hr, TEM and small angle X-ray scattering (SAXS) there were visualized particles having a mean diameter of 3.5 nm and 10% degree of polydispersion. Photoelectronic Spectroscopy (XPS) analysis indicated FeOOH formation. The microemulsion was concentrated by evaporation at 35°C and 60 torr and the wax residue obtained was redispersed in 10 ml of Polyethylene glycol (PEG). The viscosity of the solution was 9.3 cps. A coating was prepared by drawing with the velocity

of 12 mm/sec. Corning glass plates were soaked in ethanol solutions in the course of 24 hr rinsed with distilled water under sonication, then immersed in ethanol and dried at 105°C for 8 hr. A film was formed on the glass plate by spreading of the solution. After a film heat treatment at 45°C the film was not cracked or destroyed. Scanning electron microscopy (SEM) of the coating (removed from the support) did not show any growth of the particles.

Example 3

0.5 g of commercially available surfactant didodecylammonium bromide (DDAB) containing 6% of water was added to 7 ml of toluene, and stirred with shaking to form an inverse micellar solution. Thereafter 0.025 g of K_2PtCl_6 and 1.2 ml of tetraethylorthosilicate (TEOS) were added to the solution obtained, which was then stirred until the salt was fully solubilized. Then $NaBH_4$ was poured into the salt precursor solution with rapid stirring in an argon atmosphere so that the $[BH_4]:[Pt^{IV}]$ relation was 4:1. The solution gradually turned to dark brown. The pH of the solution was adjusted to 6.5 by the addition of an organic buffer in ethanol. The solution was aged at room temperature during 3 days previous to film formation by deep coating. According to sub-zero DSC data, the system did not contain any freezing water. The viscosity of the solution was 7.2 cps. A coating was prepared by drawing with the velocity of 12 mm/sec.

Glass substrates were cleaned in the same manner as described in Examples 1 and 2. In order to enhance the adhesion of the film to the glass, cleaned and dried glass supports were immersed in a 0.5% ethanol solution of triaminopropyltriethoxysilane, rinsed with dichloromethane and ethanol and baked in an oven at 120°C for 2 hr. SAXS, TEM, XPS and SEM analyses were indicative of nanosize (3-5 nm) Pt (partially oxidized on the surface) particles embedded in the silica matrix. Low temperature nitrogen adsorption of the separated film dried at 100°C in the course of 3 hr showed 37% film porosity having a mean pore diameter of 35Å. Thermo treatment of the film at 450°C for 1 hr did not change the pore characteristics of the film. Such prepared substrates were suitable in electroless Ni plating. A

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typical plating solution contained 0.105 mol of $\text{L}^+ \text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.195mol of $\text{L}^+ \text{H}_2\text{PO}_2$.

AMENDED SHEET

Claims.

1. A method for the production of nanomaterial particles (as herein defined) in which:
said nanomaterial particles are synthesized in the solutions of complex liquids from suitable precursors, which precursors are selected from suitable surfactants, metal salts, and alkoxides, by a suitable chemical reaction under mild conditions;
and preparing from said materials fine colloids dispersed in various polymer solutions.
2. A method according to Claim 1 wherein the water in the solution is non freezing water.
3. A method according to Claim 1 or 2, wherein the nanomaterial particles have a diameter of 1-5 nm.
4. A method according to any of Claims 1 to 3, wherein the mild conditons are atmospheric pressure and a temperature range of room temperature to 70°C.
5. A method according to any of Claims 1 to 4, wherein the chemical reaction is selected among a hydrolysis, reduction and exchange process.
6. A method according to any of Claims 1 to 5, wherein the solutions are selected among organized water-organic-surfactants (microemulsions and liquid crystalline media).
7. A method according to any of Claims 1 to 6, wherein the solvent is selected among suitable hydrocarbons (octane, decane, dodecane); chlorinated hydrocarbons (1,2 - dichloro-ethane); and ethers (ethylether).
8. A method according to any of Claims 1 to 7, wherein the surfactants are selected among trioctylmethyl ammonium chloride (aliquat 336), dioctyldimethylammonium bromide (DDAB), cetyltrimethylammonium chloride (CTAB); sodium bis-(2-ethyl-hexyl)- sulfosuccinate; and poly-ethoxyethylene-10-oleyl ether.
9. A method according to any of Claims 1 to 6, wherein metal oxides and precursors are selected among tetraethoxy silanes (TEOS); tetramethoxy silane (TMOS); Al, Zr iso-propoxides,;
Fe, Mg and Al chlorides; Al and Mg acetates; Na and K

orthosilicates; Zr oxychloride and transition metal salts of Fe, Co, Ni, Cu, Ru, Rh, Pd, Ir and Pt.

10. A method according to any of Claims 1 to 9, wherein the polymers are selected among polyethylene oxide (PEO); polyvinyl chloride (PVC); polyvinyl alcohol (PVA); and polymethyl methacrylate (PMMA).
11. A method according to any of Claims 5 to 10, wherein the reducing agent is selected among sodium formate; hydrogen; and certain alcohols (methanol, ethanol, isopropylalcohol).

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

29-03-2000

To:

Yitzhak, Hess & Partners
P.O.Box 6451
TEL-AVIV 61063
ISRAEL

PCT

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT
(PCT Rule 71.1)

Date of mailing
(day/month/year) 16.03.2000

Applicant's or agent's file reference
8244

IMPORTANT NOTIFICATION

International application No.
PCT/IL99/00097

International filing date (day/month/year)
16/02/1999

Priority date (day/month/year)
26/02/1998

Applicant
YISSUM RESEARCH DEVELOPMENT COMPANY OF THE..et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/

 European Patent Office
D-80298 Munich
Tel. +49 89 2399 - 0 Tx: 523656 epmu d
Fax: +49 89 2399 - 4465

Authorized officer

Gregoire, J-P

Tel. +49 89 2399-8041





PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 8244	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/IL99/00097	International filing date (day/month/year) 16/02/1999	Priority date (day/month/year) 26/02/1998
International Patent Classification (IPC) or national classification and IPC B01J13/02		
Applicant YISSUM RESEARCH DEVELOPMENT COMPANY OF THE..et al.		
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 7 sheets, including this cover sheet.</p> <p><input checked="" type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of 10 sheets.</p>		
<p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none">I <input checked="" type="checkbox"/> Basis of the reportII <input type="checkbox"/> PriorityIII <input checked="" type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicabilityIV <input type="checkbox"/> Lack of unity of inventionV <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statementVI <input type="checkbox"/> Certain documents citedVII <input type="checkbox"/> Certain defects in the international applicationVIII <input checked="" type="checkbox"/> Certain observations on the international application		
Date of submission of the demand 06/07/1999	Date of completion of this report 16.03.2000	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Gosselin, D Telephone No. +49 89 2399 8400 	

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/IL99/00097

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-9 as received on 27/02/2000 with letter of 27/02/2000

Claims, No.:

1-11 as received on 27/02/2000 with letter of 27/02/2000

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been examined in respect of:

- ☐ the entire international application.
☒ claims Nos. 2,6.

because:

- ☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (*specify*):

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/IL99/00097

- ☒ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. 2,6 are so unclear that no meaningful opinion could be formed (*specify*):

see separate sheet

- ☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed.
- ☐ no international search report has been established for the said claims Nos. .

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims
	No:	Claims 1,3-5,7,10
Inventive step (IS)	Yes:	Claims
	No:	Claims 8,9,11
Industrial applicability (IA)	Yes:	Claims 1,3-5,7-11
	No:	Claims

2. Citations and explanations

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Re Item I

The text of the description and the claims have completely revised, although the nature of the amendments was identified by reference to the application documents as originally filed, the applicant failed to indicate the support of the various amendments in the application documents as originally filed. Among these amendments, no explicit support could be found for the introduction of "in water-organic-surfactant organized solutions" into line 22 of page 3.

However, the amended claims seems to meet the requirements of Article 34.2)b) and Rule 66.8 PCT. More particularly, the addition of the terms "metal salts" in claim 1 and at the corresponding part in the description, page 4, seems to be supported by the first paragraph of page 1 as originally filed.

Re Item III

Claims 2 and 6 were not considered, because the technical features of these claims does not meet the requirements of Article 6 PCT (Cf. Item VIII).

Re Item V

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Reference is made to the following document:

D1 = WO 97 24 224 A

2. D1 discloses a process for the preparation of nanoparticles of metals. The particles are synthesised from solution of precursors, which are reacted with a reducing agent. The method involves the use of a surfactant. In view of the examples, the reaction conditions can be qualified as mild. The nanoparticles can be additionally dispersed in a polymer solution. The solvent comprises ethers and chlorinated hydrocarbons. The polymers i.a. polymethylmetacrylate. (D1: claims

more particularly claims 1, 14, 20, 21, 23 and 24).

Notwithstanding the objections under Article 6 PCT (Re Item VIII) the method according to claims 1, 3 to 5, 7 and 10 of the application lacks novelty in terms of Article 33(1) and (2) PCT over the content of D1.

3. The subject-matter of claims 8, 9 and 11 is apparently novel in view of D1. These dependent claims do not apparently contain any features which, in combination with the features of any claim to which they refer, could meet the requirements of the PCT in respect of inventive step. Such a combination could only be regarded as inventive, if the technical features of these claims should be responsible for unexpected effects or properties by comparison with the method of claims 1, 3-5, 7 and 10, which is known from D1. However, no such effects or properties are indicated in the application.

Hence, no inventive step is present in the subject-matter of claims 8, 9 and 11.

Re Item VIII

Certain observations on the international application

1. The abusive use of non conventional terms and relative terms renders the subject-matter of the claims as a whole obscure.
 - 1a. In common language, a (metal) precursor would be the starting material, which after reaction, leads to metal, metal oxide or ceramics nanoparticles. All the surfactants do not belong to this type of materials, although according to claim 1, the precursor is a compound selected among surfactants (in general) and alkoxides.

In a letter of reply dated 16.01.2000, the applicant referred to "special surfactants comprising metal ions, which are reduced (for instance, Cu, Cd sulfocinate or $(\text{PdCl}_4)(\text{R}_4\text{N})$ where (R_4N) is a quaternary ammonium cation" as metal precursors. However, these special surfactants are not referred to in the application as originally filed. According to the description, page 5, there do not even belong to

the preferred surfactants. It is finally submitted that the surfactants are not referred to as precursors in the first paragraph of page 1 of the description as originally filed.

Apparently, the terms "surfactants" seems to have been simply used in place of "metal salts" (Cf. claim 9 and page 1, first paragraph).

- 1b. In the present form, the method of claim 1 is merely defined by reference to the technical problem that the applicant intends to solve. Claim 1 does not meet the requirements of Article 6 and Rule 6 PCT in that the matter for which protection is sought is not clearly defined. The technical features "suitable" or necessary for achieving this result should be added.

By the way, the terms "as herein defined" in claim 1 should be replaced by the definition of the nanoparticles (nanomaterials) indicated in the description, page 1, first paragraph.

- 1c. It is also submitted that there is a discrepancy between the subject-matter of claim 1 and the description, page 4, lines 19-28. According to the description, the feature of claim 2 is an essential feature, which is moreover not properly defined.
- 1d. The terms "non freezing water" is not a definition commonly recognised in the art for steady state of water. Since this term is not concisely defined in the application and the publications cited in the application are not available to the examiner, claims 1 and 2 do also not meet the requirement of clarity and conciseness in view of these terms. The article of Senatra (ref.18) was not filed. The applicant did not comment how it is possible to prepare a complex liquids, where the whole water is non freezing water, and did failed to show the form of this non freezing water in the liquid. It is doubtful that a metastable state in which "non freezing water" could be present can be maintained during the method of production of nanoparticles, which necessarily involves shearing action in the dispersion.

In view of the information contained in the description, non freezing water should correspond to water molecules strongly bond to a surface. In the present case, the compounds to the surface of which the water is bounded is not identified.

- 1e. The terms "organized water-organic surfactants" or "organized-water-organic surfactants" is not understood. Microemulsions and liquid crystalline media, which are mentioned by way of example at page 4, penultimate paragraph, does not necessarily comprise an organic surfactant. The structure of such a compound and the nature of the bound with metal particles or water is not understood.

In the context of the application, the meaning of "organized" is also obscure.

It further appears that the wording of claim 6 is not consistent with that of the description, page 4, lines 38-40. Apparently one should read "organized-water-organic surfactant solutions" in claim 6 (letter of reply dated 16.01.2000).

DR. YITZHAK HESS & PARTNERS
PATENT ATTORNEYS

ד"ר יצחק הס ושותפיו
עורכי פטנטים

528 Rec'd PCT/PTO 15 AUG 2000

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סימנכם

Your Ref.

סימננו

Our Ref.

תאריך

Date

PCT/IL99/00097

8244

February 27th, 2000

BY COURRIER

AND BY FAX: 49 [89] 2399-4465

Mr. D. Gosselin
European Patent Office
Headquarters at Munich
Erhardstr. 27
D-80331 Munich
G E R M A N Y

Dear Sirs,

Re: **Patent Application No. PCT/IL99/00097**
In the name of Yissum Research Development Company of the . . . et. al.

In response to the Written Opinion of February 2nd, 2000, we advise you as follows:

1. Please disregard the new Specification annexed to our letter dated January 16th, 2000.
2. Please perform the reexamination on the basis of the following:
 - a. the answers to the Written Opinion annexed to our letter dated January 16th, 2000.
 - b. On the annexed Specification which is the original Specification as filed on February 16th, 1999, amended in accordance to the List of Amendments annexed hereto. The indication of pages and lines is based on the original Specification.

Please acknowledge receipt of this letter and enclosures by returning the copy of this letter which is also enclosed herewith.

Yours very truly,
DR. YITZHAK HESS & PARTNERS

Dr. Yitzhak Hess

encl:

LIST OF AMENDMENTS

Page 1

line 7: "metals" is replaced by "metal".

Page 3

line 22: after the words "state of water", "in water-organic-surfactant organized solutions" is added.

line 28: "water organic-surfactant" is replaced by "water-organic-surfactant".

line 33: after "strongly bound", "to the surfactant" is added.

Page 4

line 20: after the word "surfactants" is added "metal salts".

line 27: "(as determined by low temperature differential scanning calorimetry)" is added at the end.

line 36: "solvents" is replaced by "organic solvents".

Page 5

line 1: "enables" is replaced by "enable"

line 10: the word "Metal" is cancelled.

line 12: "triethoxy and trimethoxy" is replaced by "tetraethoxy and tetramethoxy....".

Page 8

line 5: after the word "surfactants" is added "metal salts".

lines 21-22: "water organic surfactant" is replaced by "water-organic-surfactant".

lines 33-34: "metal" is cancelled and "triethoxy and trimethoxy" is replaced by "tetraethoxy and tetramethoxy".

From the INTERNATIONAL BUREAU

PCT

**NOTIFICATION OF RECEIPT OF
RECORD COPY**

(PCT Rule 24.2(a))

To:

HESS, Yitzhak
Dr. Yitzhak Hess & Partners
P.O. Box 6451
61063 Tel Aviv
ISRAËL

Date of mailing (day/month/year) 23 March 1999 (23.03.99)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference 8244	International application No. PCT/IL99/00097

The applicant is hereby notified that the International Bureau has received the record copy of the international application as detailed below.

Name(s) of the applicant(s) and State(s) for which they are applicants:

YISSUM RESEARCH DEVELOPMENT COMPANY OF THE HEBREW UNIVERSITY OF JERUSALEM (for
all designated States except US)
GARTI, Nissim et al (for US)

International filing date : 16 February 1999 (16.02.99)
Priority date(s) claimed : 26 February 1998 (26.02.98)
Date of receipt of the record copy
by the International Bureau : 11 March 1999 (11.03.99)
List of designated Offices :

AP : GH, GM, KE, LS, MW, SD, SZ, UG, ZW
EA : AM, AZ, BY, KG, KZ, MD, RU, TJ, TM
EP : AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE
OA : BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG
National : AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO,
NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW

ATTENTION

The applicant should carefully check the data appearing in this Notification. In case of any discrepancy between these data and the indications in the international application, the applicant should immediately inform the International Bureau.

In addition, the applicant's attention is drawn to the information contained in the Annex, relating to:

- ☒ time limits for entry into the national phase
- ☐ confirmation of precautionary designations
- ☒ requirements regarding priority documents

A copy of this Notification is being sent to the receiving Office and to the International Searching Authority.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No. (41-22) 740.14.35	Authorized officer: Ting Zhao Telephone No. (41-22) 338.83.38
---	---



INFORMATION ON TIME LIMITS FOR ENTERING THE NATIONAL PHASE

The applicant is reminded that the "national phase" must be entered before each of the designated Offices indicated in the Notification of Receipt of Record Copy (Form PCT/IB/301) by paying national fees and furnishing translations, as prescribed by the applicable national laws.

The time limit for performing these procedural acts is **20 MONTHS** from the priority date or, for those designated States which the applicant elects in a demand for international preliminary examination or in a later election, **30 MONTHS** from the priority date, provided that the election is made before the expiration of 19 months from the priority date. Some designated (or elected) Offices have fixed time limits which expire even later than 20 or 30 months from the priority date. In other Offices an extension of time or grace period, in some cases upon payment of an additional fee, is available.

In addition to these procedural acts, the applicant may also have to comply with other special requirements applicable in certain Offices. It is the applicant's responsibility to ensure that the necessary steps to enter the national phase are taken in a timely fashion. Most designated Offices do not issue reminders to applicants in connection with the entry into the national phase.

For detailed information about the procedural acts to be performed to enter the national phase before each designated Office, the applicable time limits and possible extensions of time or grace periods, and any other requirements, see the relevant Chapters of Volume II of the PCT Applicant's Guide. Information about the requirements for filing a demand for international preliminary examination is set out in Chapter IX of Volume I of the PCT Applicant's Guide.

GR and ES became bound by PCT Chapter II on 7 September 1996 and 6 September 1997, respectively, and may, therefore, be elected in a demand or a later election filed on or after 7 September 1996 and 6 September 1997, respectively, regardless of the filing date of the international application. (See second paragraph above.)

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

CONFIRMATION OF PRECAUTIONARY DESIGNATIONS

This notification lists only specific designations made under Rule 4.9(a) in the request. It is important to check that these designations are correct. Errors in designations can be corrected where precautionary designations have been made under Rule 4.9(b). The applicant is hereby reminded that any precautionary designations may be confirmed according to Rule 4.9(c) before the expiration of 15 months from the priority date. If it is not confirmed, it will automatically be regarded as withdrawn by the applicant. There will be no reminder and no invitation. Confirmation of a designation consists of the filing of a notice specifying the designated State concerned (with an indication of the kind of protection or treatment desired) and the payment of the designation and confirmation fees. Confirmation must reach the receiving Office within the 15-month time limit.

REQUIREMENTS REGARDING PRIORITY DOCUMENTS

For applicants who have not yet complied with the requirements regarding priority documents, the following is recalled:

Where the priority of an earlier national, regional or international application is claimed, the applicant must submit a copy of the said earlier application, certified by the authority with which it was filed ("the priority document") to the receiving Office (which will transmit it to the International Bureau) or directly to the International Bureau, before the expiration of 16 months from the priority date, provided that any such priority document may still be submitted to the International Bureau before that date of international publication of the international application, in which case that document will be considered to have been received by the International Bureau on the last day of the 16-month time limit (Rule 17.1(a)).

Where the priority document is issued by the receiving Office, the applicant may, instead of submitting the priority document, request the receiving Office to prepare and transmit the priority document to the International Bureau. Such request must be made before the expiration of the 16-month time limit and may be subjected by the receiving Office to the payment of a fee (Rule 17.1(b)).

If the priority document concerned is not submitted to the International Bureau or if the request to the receiving Office to prepare and transmit the priority document has not been made (and the corresponding fee, if any, paid) within the applicable time limit indicated under the preceding paragraphs, any designated State may disregard the priority claim, provided that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity to furnish the priority document within a time limit which is reasonable under the circumstances.

Where several priorities are claimed, the priority date to be considered for the purposes of computing the 16-month time limit is the filing date of the earliest application whose priority is claimed.

PATENT COOPERATION TREATY

1039

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION CONCERNING SUBMISSION OR TRANSMITTAL OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

To:

HESS, Yitzhak
Dr. Yitzhak Hess & Partners
P.O. Box 6451
61063 Tel Aviv
ISRAËL

Date of mailing (day/month/year) 30 March 1999 (30.03.99)	
Applicant's or agent's file reference 8244	IMPORTANT NOTIFICATION
International application No. PCT/IL99/00097	International filing date (day/month/year) 16 February 1999 (16.02.99)
International publication date (day/month/year) Not yet published	Priority date (day/month/year) 26 February 1998 (26.02.98)
Applicant YISSUM RESEARCH DEVELOPMENT COMPANY OF THE HEBREW UNIVERSITY OF JERUSALEM et al	

1. The applicant is hereby notified of the date of receipt (except where the letters "NR" appear in the right-hand column) by the International Bureau of the priority document(s) relating to the earlier application(s) indicated below. Unless otherwise indicated by an asterisk appearing next to a date of receipt, or by the letters "NR", in the right-hand column, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).
2. This updates and replaces any previously issued notification concerning submission or transmittal of priority documents.
3. An asterisk(*) appearing next to a date of receipt, in the right-hand column, denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b). In such a case, **the attention of the applicant is directed** to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.
4. The letters "NR" appearing in the right-hand column denote a priority document which was not received by the International Bureau or which the applicant did not request the receiving Office to prepare and transmit to the International Bureau, as provided by Rule 17.1(a) or (b), respectively. In such a case, **the attention of the applicant is directed** to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

<u>Priority date</u>	<u>Priority application No.</u>	<u>Country or regional Office or PCT receiving Office</u>	<u>Date of receipt of priority document</u>
26 Febr 1998 (26.02.98)	123468	IL	17 Marc 1999 (17.03.99)

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Carlos Naranjo
Facsimile No. (41-22) 740.14.35	Telephone No. (41-22) 338.83.38

CAN

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

To:

Yitzhak, Hess & Partners
P.O.Box 6451
TEL-AVIV 61063
ISRAEL

NOTIFICATION OF RECEIPT
OF SEARCH COPY

(PCT Rule 25.1)

Date of mailing
(day/month/year)

27/04/1999

Applicant's or agent's file reference

8244

IMPORTANT NOTIFICATION

International application No.

PCT/IL 99/00097

International filing date (day/month/year)

16/02/1999

Priority date (day/month/year)

26/02/1998

Applicant

YISSUM RESEARCH DEVELOPMENT COMPANY OF THE HEBREW;

1. Where the International Searching Authority and the Receiving Office are not the same office:

The applicant is hereby notified that the search copy of the international application was received by this International Searching Authority on the date indicated below.

Where the International Searching Authority and the Receiving Office are the same office:

The applicant is hereby notified that the search copy of the international application was received on the date indicated below.

16/03/1999 (date of receipt).

2. ☐ The search copy was accompanied by a nucleotide and/or amino acid sequence listing in computer readable form.

3. Time limit for establishment of International Search Report

The applicant is informed that the time limit for establishing the International Search Report is 3 months from the date of receipt indicated above or 9 months from the priority date, whichever time limit expires later

4. A copy of this notification has been sent to the International Bureau and, where the first sentence of paragraph 1 applies, to the Receiving Office.

Name and mailing address of the International Searching Authority



European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

ISA/EP

ENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL SEARCH REPORT
OR THE DECLARATION

(PCT Rule 44.1)

310 MAY 1999

To:

Yitzhak, Hess & Partners
P.O.Box 6451
TEL-AVIV 61063
ISRAEL

Date of mailing
(day/month/year)

21/05/1999

Applicant's or agent's file reference

8244

FOR FURTHER ACTION

See paragraphs 1 and 4 below

International application No.

PCT/IL 99/ 00097

International filing date
(day/month/year)

16/02/1999

Applicant

YISSUM RESEARCH DEVELOPMENT COMPANY OF THE HEBREW;

1. ☒ The applicant is hereby notified that the International Search Report has been established and is transmitted herewith.

Filing of amendments and statement under Article 19:

The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.

Where? Directly to the International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland
Fascimile No.: (41-22) 740.14.35

For more detailed instructions, see the notes on the accompanying sheet.

2. ☐ The applicant is hereby notified that no International Search Report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. ☐ **With regard to the protest** against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Further action(s):** The applicant is reminded of the following:

Shortly after **18 months** from the priority date, the international application will be published by the International Bureau.

If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90bis.1 and 90bis.3, respectively, before the completion of the technical preparations for international publication.

Within **19 months** from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

Within **20 months** from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 19 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the International Searching Authority



European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel. (+31-70) 340-2040. Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Patrick Gehl

These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions respectively.

INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only.

What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

When?

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

How?

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

What documents must/may accompany the amendments?

Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

- (i) the claim is unchanged;
- (ii) the claim is cancelled;
- (iii) the claim is new;
- (iv) the claim replaces one or more claims as filed;
- (v) the claim is the result of the division of a claim as filed.

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."
2. [Where originally there were 15 claims and after amendment of all claims there are 11]:
"Claims 1 to 15 replaced by amended claims 1 to 11."
3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."
4. [Where various kinds of amendments are made]:
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

"Statement under article 19(1)" (Rule 46.4)

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

It must be in the language in which the international application is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

Consequence if a demand for international preliminary examination has already been filed

If, at the time of filing any amendments under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the same time of filing the amendments with the International Bureau, also file a copy of such amendments with the International Preliminary Examining Authority (see Rule 62.2(a), first sentence).

Consequence with regard to translation of the international application for entry into the national phase

The applicant's attention is drawn to the fact that, where upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see Volume II of the PCT Applicant's Guide.

MAIL: P.O.B. 6451 TEL-AVIV 61063 תל-אביב, 6451 דואר: ת.ד.
OFFICE: 279, HAYARKON ST. TEL-AVIV 63504 תל-אביב 279, משרד: רח' הירקון
PHONE: 972-3-604-2715 טלפון:
FAX: 972-3-546-8038 פקס:
E-MAIL: hess@mail.inter.net.il דואר אלקטרוני:

סימנכם
Your Ref.

סימננו
Our Ref.

תאריך
Date

8244

June 30, 1999

EUROPEAN PATENT OFFICE
D-80298 MUNICH
GERMANY

Dear Sirs,

Re; PCT Application PCT/IL 99/00097
Yissum Research Development Company
of the Hebrew University of Jerusalem et al

We enclose herewith:

1. Demand Form PCT/IPEA/401 - 3 pages
2. Fee Calculation Sheet - Form PCT/IPEA/401(annex)
3. Cheque in amount of DM 3290.-
4. Confirmation page

Please acknowledge receipt of these documents by returning the attached confirmation page.

Yours very truly
DR. YITZHAK HESS & PARTNERS

Cila Hess-Milutin

Copies: WIPO
Israeli Patent Office

The demand must be filed directly with the competent International Preliminary Examining Authority. If two or more Authorities are competent, with the one chosen by the applicant. The full name or two-letter code of that Authority may be indicated by the applicant on the line below:

IPEA/ _____

PCT

CHAPTER II

DEMAND

under Article 31 of the Patent Cooperation Treaty:
The undersigned requests that the international application specified below be the subject of international preliminary examination according to the Patent Cooperation Treaty and hereby elects all eligible States (except where otherwise indicated).

For International Preliminary Examining Authority use only		
Identification of IPEA		Date of receipt of DEMAND
Box No. I IDENTIFICATION OF THE INTERNATIONAL APPLICATION		Applicant's or agent's file reference 8244
International application No. PCT/IL 99/00097	International filing date (day/month/year) 16.02.1999	(Earliest) Priority date (day/month/year) 26.02.1998
Title of invention METHOD FOR THE PREPARATION OF NANOSIZED MATERIAL PARTICLES		
Box No. II APPLICANT(S)		
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) YISSUM RESEARCH DEVELOPMENT COMPANY OF THE HEBREW UNIVERSITY OF JERUSALEM P.O.B. 4279 JERUSALEM 91042, ISRAEL		Telephone No.:
		Facsimile No.:
		Teleprinter No.:
State (that is, country) of nationality: ISRAEL		State (that is, country) of residence: ISRAEL
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) GARTI NISSIM 9 Derech Hachoshesh St. Ramot, JERUSALEM ISRAEL		
State (that is, country) of nationality: ISRAEL		State (that is, country) of residence: ISRAEL
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) BERCOVICH YANA 309/20 HaAnafa St. JERUSALEM 93902 ISRAEL		
State (that is, country) of nationality: ISRAEL		State (that is, country) of residence: ISRAEL
<input type="checkbox"/> Further applicants are indicated on a continuation sheet.		

Box No. III AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCEThe following person is ☒ agent ☐ common representativeand ☒ has been appointed earlier and represents the applicant(s) also for international preliminary examination.☐ is hereby appointed and any earlier appointment of (an) agent(s)/common representative is hereby revoked.☐ is hereby appointed, specifically for the procedure before the International Preliminary Examining Authority, in addition to the agent(s)/common representative appointed earlier.Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*DR. YITZHAK HESS & PARTNERS and/or DR. HESS YITZHAK
and/or HESS-MILUTIN CILA
P.O.B. 6451 TEL-AVIV 61063, ISRAEL

Telephone No.:

03-6042715

Facsimile No.:

03-5468038

Teleprinter No.:

☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.**Box No. IV BASIS FOR INTERNATIONAL PRELIMINARY EXAMINATION****Statement concerning amendments:***

1. The applicant wishes the international preliminary examination to start on the basis of:

☒ the international application as originally filedthe description ☒ as originally filed☐ as amended under Article 34the claims ☒ as originally filed☐ as amended under Article 19 (together with any accompanying statement)☐ as amended under Article 34the drawings ☒ as originally filed☐ as amended under Article 342. ☐ The applicant wishes any amendment to the claims under Article 19 to be considered as reversed.3. ☐ The applicant wishes the start of the international preliminary examination to be postponed until the expiration of 20 months from the priority date unless the International Preliminary Examining Authority receives a copy of any amendments made under Article 19 or a notice from the applicant that he does not wish to make such amendments (Rule 69.1(d)). *(This check-box may be marked only where the time limit under Article 19 has not yet expired.)*

* Where no check-box is marked, international preliminary examination will start on the basis of the international application as originally filed or, where a copy of amendments to the claims under Article 19 and/or amendments of the international application under Article 34 are received by the International Preliminary Examining Authority before it has begun to draw up a written opinion or the international preliminary examination report, as so amended.

Language for the purposes of international preliminary examination: ENGLISH☒ which is the language in which the international application was filed.☐ which is the language of a translation furnished for the purposes of international search.☐ which is the language of publication of the international application.☐ which is the language of the translation (to be) furnished for the purposes of international preliminary examination.**Box No. V ELECTION OF STATES**The applicant hereby elects all eligible States *(that is, all States which have been designated and which are bound by Chapter II of the PCT)*

excluding the following States which the applicant wishes not to elect:

Box No. VI CHECK LIST

The demand is accompanied by the following elements, in the language referred to in Box No. IV, for the purposes of international preliminary examination:

- | | | |
|--|---|--------|
| 1. translation of international application | : | sheets |
| 2. amendments under Article 34 | : | sheets |
| 3. copy (or, where required, translation) of amendments under Article 19 | : | sheets |
| 4. copy (or, where required, translation) of statement under Article 19 | : | sheets |
| 5. letter | : | sheets |
| 6. other (<i>specify</i>) | : | sheets |

For International Preliminary
Examining Authority use only

received not received

<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>

The demand is also accompanied by the item(s) marked below:

- | | |
|--|---|
| 1. <input checked="" type="checkbox"/> fee calculation sheet | 4. <input type="checkbox"/> statement explaining lack of signature |
| 2. <input type="checkbox"/> separate signed power of attorney | 5. <input type="checkbox"/> nucleotide and or amino acid sequence listing in computer readable form |
| 3. <input type="checkbox"/> copy of general power of attorney; reference number, if any: | 6. <input checked="" type="checkbox"/> other (<i>specify</i>): CHEQUE |

Box No. VII SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the demand).

CILA HESS-MILUTIN
PARTNER OF DR. YITZHAK HESS & PARTNERS

For International Preliminary Examining Authority use only

1. Date of actual receipt of DEMAND:

2. Adjusted date of receipt of demand due to CORRECTIONS under Rule 60.1(b):

3. ☐ The date of receipt of the demand is AFTER the expiration of 19 months from the priority date and item 4 or 5, below, does not apply.

☐ The applicant has been informed accordingly.

4. ☐ The date of receipt of the demand is WITHIN the period of 19 months from the priority date as extended by virtue of Rule 80.5.

5. ☐ Although the date of receipt of the demand is after the expiration of 19 months from the priority date, the delay in arrival is EXCUSED pursuant to Rule 82.

For International Bureau use only

Demand received from IPEA on:

PCT

FEE CALCULATION SHEET

Annex to the Demand for international preliminary examination

International application No. PCT/IL 99/00097	For International Preliminary Examining Authority use only									
Applicant's or agent's file reference 8244	Date stamp of the IPEA									
Applicant YISSUM RESEARCH DEVELOPMENT COMPANY OF THE HEBREW UNIVERSITY OF JERUSALEM et al.										
Calculation of prescribed fees										
1. Preliminary examination fee	3000 DM	<input type="checkbox"/> P								
2. Handling fee (<i>Applicants from certain States are entitled to a reduction of 75% of the handling fee. Where the applicant is (or all applicants are) so entitled, the amount to be entered at H is 25% of the handling fee.</i>)	290 DM	<input type="checkbox"/> H								
3290 DM										
3. Total of prescribed fees Add the amounts entered at P and H and enter total in the TOTAL box	<div style="border: 1px solid black; padding: 5px; width: 150px; margin: 0 auto;">TOTAL</div>									
Mode of Payment										
<table style="width: 100%;"> <tr> <td><input type="checkbox"/> authorization to charge deposit account with the IPEA (see below)</td> <td><input type="checkbox"/> cash</td> </tr> <tr> <td><input checked="" type="checkbox"/> cheque</td> <td><input type="checkbox"/> revenue stamps</td> </tr> <tr> <td><input type="checkbox"/> postal money order</td> <td><input type="checkbox"/> coupons</td> </tr> <tr> <td><input type="checkbox"/> bank draft</td> <td><input type="checkbox"/> other (specify):</td> </tr> </table>			<input type="checkbox"/> authorization to charge deposit account with the IPEA (see below)	<input type="checkbox"/> cash	<input checked="" type="checkbox"/> cheque	<input type="checkbox"/> revenue stamps	<input type="checkbox"/> postal money order	<input type="checkbox"/> coupons	<input type="checkbox"/> bank draft	<input type="checkbox"/> other (specify):
<input type="checkbox"/> authorization to charge deposit account with the IPEA (see below)	<input type="checkbox"/> cash									
<input checked="" type="checkbox"/> cheque	<input type="checkbox"/> revenue stamps									
<input type="checkbox"/> postal money order	<input type="checkbox"/> coupons									
<input type="checkbox"/> bank draft	<input type="checkbox"/> other (specify):									
Deposit Account Authorization (<i>this mode of payment may not be available at all IPEAs</i>)										
The IPEA/ _____ <input type="checkbox"/> is hereby authorized to charge the total fees indicated above to my deposit account.										
<input type="checkbox"/> (<i>this check-box may be marked only if the conditions for deposit accounts of the IPEA so permit</i>) is hereby authorized to charge any deficiency or credit any overpayment in the total fees indicated above to my deposit account.										
Deposit Account Number _____	Date (day/month/year) _____	Signature _____								

בנק לוי ישראלי



AIR MAIL REGISTERED

TRUMPELDOR

Mail to
GERMANY

Date 01 JULY 99

Dear sir,

125382

We have received your cheque with our cheque No.

OTANUSANLAGE 12-21, W - 6000 FRANKFURT/MAIN 1

By order of YITZHAK HESS

The sum of
DEM *****3,290.00#

Particulars

bank leumi בנק לוי



807-125382

AGAINST THIS CHEQUE

DATE: 01 JULY 99

Pay to EUROPEAN PATENT OFFICE

THREE THOUSAND TWO HUNDRED NINETY

The sum of

DEM *****3,290.00#

DEUTSCHE BANK AG

TOTANUSANLAGE 12-21, W - 6000 FRANKFURT/MAIN 1

AC. 953604601

BANK LEUMI LE-ISRAEL B.M.

TRUMPELDOR

A. Krasovits
A. Krasovits
G. Gureld
1177



הצהרה בדבר תשלום לתושב חוץ ובקשה להקטנת ניכר ממס במקור
לפי סעיפים 161-170 לפקודת מס הכנסה

אני, החתום מטה, מבקש כי על תשלוס בסך

סוכים במיליון	סוג מטבע
3290	DM

שנאי מעלם לחיובב חוץ עפריטיו רשמים לרלן, יחול ניכוי מס רבנסה במקור בשיעור של 0% מררח רחשלאס (נימקי רבנסה)

.....
PCT/IL 99/00097 בקשת

פרטי המשלם ומהות התשלום

[illegible]

פרטים על מדות הדפדפנות/התשלום לחשבון חוץ אצל המעלים (הוצאה עסקית, החזר הוצאות עסקיות, הוצאה פרטית, אחר)

הוצאה עסקית

פרטי המקבל ופרטי החשבון (אליו מועבר התשלום)

D-80298 Munchen, Germany			
EUROPEAN PATENT OFFICE			
מס' חשבוני / שם החברה			
רחוב			
מספר			
עיר			
מילוד			
שם הבנק			
רחוב			
מס' חשבוני / שם החברה			
רחוב			
מספר			
עיר			
מילוד			

רמסמכים ומצורפים לאימות הבקשה

חשבון

בוצע חשלוס קודם למקבל בשנת ה'תס"ח (סמן ✓ בריבוע המתאים)

רמס שטערלס	סוג רמטבע	רמריח	רמכום (ברוטו למי ימי חם)	רמאירן רמטשום	רמ כן רמס

27

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לְיִמִּים יְחָסִים מִיּוֹחָדִים בֵּין רַמְשֶׁלֶס לַמֶּלֶךְ

כן (פרט)

27 ☒

הצהרת המשלם

הריני מצהיר בזאת כי הפרטים שבטופס זה הינם מלאים ונכונים				
1 ביולי 1999		ד"ר יצחק חס ושותפיו		עו"פ
חתימך	שם	חפיקך	חתימה	חותמת

* מחק את הבלתי מתאים

נוודה לכם אם תמציאו לנו המחאה בנקאית בהתאם לנתונים הניתנים לעיל

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

26-09-1997

PCT

To:

Yitzhak, Hess & Partners
P.O.Box 6451
TEL-AVIV 61063
ISRAEL

NOTIFICATION OF RECEIPT OF DEMAND BY COMPETENT INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

(PCT Rules 59.3(e) and 61.1(b), first sentence
and Administrative Instructions, Section 601(a))

Date of mailing
(day/month/year)

20.09.99

Applicant's or agent's file reference
8244

IMPORTANT NOTIFICATION

International application No.

PCT/IL 99/00097

International filing date (day/month/year)

16/02/1999

Priority date (day/month/year)

26/02/1998

Applicant

YISSUM RESEARCH DEVELOPMENT COMPANY OF THE..et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority considers the following date as the date of receipt of the demand for international preliminary examination of the international application:

06/07/1999

2. This date of receipt is:

- ☒ the actual date of receipt of the demand by this Authority (Rule 61.1(b)).
- ☐ the actual date of receipt of the demand on behalf of this Authority (Rule 59.3(e)).
- ☐ the date on which this Authority has, in response to the invitation to correct defects in the demand (Form PCT/IPEA/404), received the required corrections.

3. ☐ **ATTENTION:** That date of receipt is **AFTER** the expiration of 19 months from the priority date. Consequently, the election(s) made in the demand does (do) not have the effect of postponing the entry into the national phase until 30 months from the priority date (or later in some Offices) (Article 39(1)). Therefore, the acts for entry into the national phase must be performed within 20 months from the priority date (or later in some Offices) (Article 22). For details, see the *PCT Applicant's Guide*, Volume II.

- ☐ (If applicable) This notification confirms the information given by telephone, facsimile transmission or in person on:

4. Only where paragraph 3 applies, a copy of this notification has been sent to the International Bureau.

Name and mailing address of the IPEA/



European Patent Office
D-80298 Munich
Tel. (+49-89) 2399-0, Tx: 523656 epmu d
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Authorized officer

Jasper Heil

Telephone No.

-28 79



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: B01J 13/02	A1	(11) International Publication Number: WO 99/43427 (43) International Publication Date: 2 September 1999 (02.09.99)
(21) International Application Number: PCT/IL99/00097 (22) International Filing Date: 16 February 1999 (16.02.99) (30) Priority Data: 123468 26 February 1998 (26.02.98) IL (71) Applicant (for all designated States except US): YISSUM RESEARCH DEVELOPMENT COMPANY OF THE HE- BREW UNIVERSITY OF JERUSALEM [IL/IL]; P.O. Box 4279, 91042 Jerusalem (IL). (72) Inventors; and (75) Inventors/Applicants (for US only): GARTI, Nissim [IL/IL]; Derech Hachosh Street 9, Ramot, 95225 Jerusalem (IL). BERKOVICH, Yana [IL/IL]; HaAnafa Street 309/20, 93902 Jerusalem (IL). (74) Agents: HESS, Yitzhak et al.; Dr. Yitzhak Hess & Partners, P.O. Box 6451, 61063 Tel Aviv (IL).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: METHODS FOR THE PREPARATION OF NANOSIZED MATERIAL PARTICLES		
(57) Abstract <p>The present invention relates to a method for the production of particles of nano-materials being transition metals and alloys; metal oxides; and ceramic compositions having a small nanosize, i.e. about 1 – 6 nm. The method comprises a synthesis in the solutions of complex liquids from suitable precursors, which precursors are selected from suitable surfactants and alkoxides, by a suitable chemical reaction under mild conditions; and preparing from said materials fine colloids dispersed in various polymer solutions. The water in the solution is preferably non freezing water, the mild conditions are atmospheric pressure and a temperature range of room temperature to 70 °C, and the reaction condition is selected among a hydrolysis, reduction and exchange process.</p>		

METHODS FOR THE PREPARATION OF NANOSIZED MATERIAL PARTICLES

The present invention relates to the methods for the preparation of nanosized material particles. ("Nano-materials" in connection with the present invention comprise transition metals and alloys; metal oxides; and ceramic compositions having a small nanosize, i.e. about 1 - 6 nm.) Nanomaterials are prepared from the corresponding precursors i.e. the corresponding metals salts or alkoxides by suitable chemical reactions, e.g. reduction, hydrolysis and exchange processes under mild conditions.

There are known methods to prepare clusters or fine colloids from said nanomaterials which are dispersed in different suitable solutions. Appropriate liquid media enable the production of different preparations, which may be used as thin films on various supports.

There are known several methods for the preparation of ultrathin films of metal particles on solid supports, e.g. ion implantation (M.Che. C.O. Bennet, Adv. Catal. 1989, 36, 55); organometallic chemical vapor deposition (A. Sherman, Chemical Vapor Deposition for Microelectronics, Principles, Technology and Application, Noyes Publications; Park Ridge, N.J. 1987; and N.H. Dryden et. al., Chem. Mater. 1991, 3, 677); metal deposition from colloidal solution (G.Schmid, Chem. Rev. 1992, 92, 1709); reductive metal deposition from aqueous salt solution (I.Coulthard, et. al., Langmuir 1993, 9, 3441.); photodecomposition of metal complexes in thin films (R.Krasnasky et. al. Langmuir, 1991, 7, 2881); and photo-reductive deposition from Pd(II) complexes in solution (K. Kondo et. al., Chem. Lett. 1992, 999). Other technics are based on the film formation of noble metal loaded block copolymers (Y.NgCheongChan et. al., Chem.Mater. 1992, 4, 24; and J.P.Spatz, et al., Adv. Mater. 1995, 7, 731.); on the Langmuir-Blodgett (LB) transfer of monolayers or surfactant stabilized metal colloids (F.S. Meldrum et. al., Langmuir 1994, 10, 2035; and F.S. Meldrum et al., Chem. Mater. 1995, 7, 1112); and on thermal decomposition of LB films of zero valent palladium complexes (E.

overcome said disadvantages, i.e should not be complicated, not be too expensive and yield nanomaterial particles having the desired size.

It is well known that water which appears to be a key factor which governs the association of surfactants in different solvents, functions not only as an inert solvent but plays a significant part in the mechanism of chemical processes. (Garti et. al. Coll. & Interface Sci. 178 (1996) p. 60-68). When describing the state of water in relation to any surface a distinction is usually made between "bulk" and "bound" water. It is assumed that "bulk" or free water has physico-chemical properties which are not very different from those of pure water. "Bound" water may be defined by the operational definitions which refer to the water detected by a certain technique.

According to the method utilized by Senatra (D. Senatra et. al. Can. J. of Phys. 68 (1990) p. 1041), in which the endothermic scaling mode was applied and the peaks representing various states of water were identified and analyzed, it was shown that "free" water melts at 0°C, "interfacial bound" water melts at -10°C, and non-freezing water which is the most strongly bound part of bound water has no peaks on thermograms up to -100°C.

It has been found that the state of the water is strictly correlated with the size of the particles. Particles which have a diameter of less than 5 nm are synthesized in systems which comprise only strongly bound water (non freezing water according to subzero differential scanning Calorimetry DSC).

In developing the method according to the present invention it has been considered:

- a. producing the water organic-surfactant organized solutions (complex liquids) comprising nanosized particles in particular having a diameter of 1- 5 nm which are useful for the particle preparation;
- b. regulating the water content in such a manner that the whole water will be strongly bound (non-freezing) in the system, thus enabling to provide nano particles which have a diameter of less than 5 nm;
- c. the regulation of the solution structures which enables the regulation of the morphology of the particles;

The appropriate liquid media enables the preparation of different self assemblies of nanomaterials and subsequently the use of them as thin films on various supports.

Suitable surfactants are, for example,:

Quaternary ammonium salts, e.g. trioctylmethyl ammonium chloride (aliquat 336), dioctyldimethylammonium bromide (DDAB), cetyltrimethylammonium chloride (CTAB), etc.; sodium bis-(2-ethyl-hexyl)- sulfosuccinate; poly-ethoxyethylene-10-oley ether (Btj 96; etc.

Metal oxide precursors may be, e.g.

alkoxides:

triethoxy silane (TEOS); trimethoxy silane (TMOS); Al, Zr isopropoxides, etc;

Fe, Mg and Al chlorides; Al and Mg acetates; Na and K orthosilicates; Zr oxychloride; etc. Metal precursors may be, e.g. transition metal salts of Fe, Co, Ni, Cu, Ru, Rh, Pd, Ir and Pt, e.g. FeCl_3 , K_2PdCl_4 , K_2PtCl_4 and CuCl_2 .

The polymers may be selected, e.g. from polyethylene oxide (PEO), polyvinyl chloride (PVC), polyvinyl alcohol (PVA), polymethyl methacrylate (PMMA), etc.

Suitable reducing agents are, for example, sodium formate; hydrogen; certain alcohols (methanol, ethanol, isopropylalcohol); etc.

The method according to the present invention can direct the morphology, dimension and homogeneity of the size distributions of the small colloids (and clusters) and also their self assembling.

Example 1

A Pd colloidal dispersion was prepared from a solution containing 12% wt of hydrated trioctylmethylammonium chloride (aliquat 336) which corresponds to water/aliquat molar ratio = 3.06. Sub-zero DSC analysis did not reveal any peak which belongs to interfacial (-10°C) and free water (0°C) in the precursor solution.

Potassium tetrachloropalladate (K_2PdCl_4) (326mg) was solubilized in a 5 ml aliquat-dichloroethane-water mixture. Sodium formate (NaHCO_2) (0.22 gr) was poured onto the mixture under argon. The reaction was carried out in accordance with the

under sonication, then immersed in ethanol and dried at 105°C for 8 hr. A film was formed on the glass plate by spreading of the solution. After a film heat treatment at 45°C the film was not cracked or destroyed. Scanning electron microscopy (SEM) of the coating (removed from the support) did not show any growth of the particles.

Example 3

0.5 g of commercially available surfactant didodecylammonium bromide (DDAB) containing 6% of water was added to 7 ml of toluene, and stirred with shaking to form an inverse micellar solution. Thereafter 0.025 g of K_2PtCl_6 and 1.2 ml of tetraethyloxysilicate (TEOS) were added to the solution obtained, which was then stirred until the salt was fully solubilized. Then $NaBH_4$ was poured into the salt precursor solution with rapid stirring in an argon atmosphere so that the $[BH_4]:[Pt^{4+}]$ relation was 4:1. The solution gradually turned to dark brown. The pH of the solution was adjusted to 6.5 by the addition of an organic buffer in ethanol. The solution was aged at room temperature during 3 days previous to film formation by deep coating. According to sub-zero DSC data, the system did not contain any freezing water. The viscosity of the solution was 7.2 cps. A coating was prepared by drawing with the velocity of 12 mm/sec.

Glass substrates were cleaned in the same manner as described in Examples 1 and 2. In order to enhance the adhesion of the film to the glass, cleaned and dried glass supports were immersed in a 0.5% ethanol solution of triaminopropyltriethoxysilane, rinsed with dichloromethane and ethanol and baked in an oven at 120°C for 2 hr. SAXS, TEM, XPS and SEM analyses were indicative of nanosize (3-5 nm) Pt (partially oxidized on the surface) particles embedded in the silica matrix. Low temperature nitrogen adsorption of the separated film dried at 100°C in the course of 3 hr showed 37% film porosity having a mean pore diameter of 35Å. Thermo treatment of the film at 450°C for 1 hr did not change the pore characteristics of the film. Such prepared substrates were suitable in electroless Ni plating. A typical plating solution contained 0.105 mol of $L^{-1} NiSO_4 \cdot 7H_2O$ and 0.195mol of $L^{-1} H_2PO_2$.

Fe, Co, Ni, Cu, Ru, Rh, Pd, Ir and Pt.

10. A method according to any of Claims 1 to 9, wherein the polymers are selected among polyethylene oxide (PEO); polyvinyl chloride (PVC); polyvinyl alcohol (PVA); and polymethyl methacrylate (PMMA).
11. A method according to any of Claims 5 to 10, wherein the reducing agent is selected among sodium formate; hydrogen; and certain alcohols (methanol, ethanol, isopropylalcohol).

INTERNATIONAL SEARCH REPORT

International Application No

PCT/IL 99/00097

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B01J13/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 24224 A (HEATH J.R. ET AL) 10 July 1997 see claims 1-30 -----	1, 3, 5, 7, 8, 10

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

12 May 1999

Date of mailing of the international search report

21/05/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Fouquier, J-P

PCT

NOTICE INFORMING THE APPLICANT OF THE COMMUNICATION OF THE INTERNATIONAL APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

From the INTERNATIONAL BUREAU

To:

HESS, Yitzhak
Dr. Yitzhak Hess & Partners
P.O. Box 6451
61063 Tel Aviv
ISRAËL

Date of mailing (day/month/year)
02 September 1999 (02.09.99)

Applicant's or agent's file reference
8244

IMPORTANT NOTICE

International application No.
PCT/IL99/00097

International filing date (day/month/year)
16 February 1999 (16.02.99)

Priority date (day/month/year)
26 February 1998 (26.02.98)

Applicant
YISSUM RESEARCH DEVELOPMENT COMPANY OF THE HEBREW UNIVERSITY OF
JERUSALEM et al

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice:
AU,CN,EP,IL,JP,KP,KR,US

In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:

AL,AM,AP,AT,AZ,BA,BB,BG,BR,BY,CA,CH,CU,CZ,DE,DK,EA,EE,ES,FI,GB,GD,GE,GH,GM,HR,HU,
ID,IN,IS,KE,KG,KZ,LC,LK,LR,LS,LT,LU,LV,MD,MG,MK,MN,MW,MX,NO,NZ,OA,PL,PT,RO,RU,SD,
SE,SG,SI,SK,SL,TJ,TM,TR,TT,UA,UG,UZ,VN,YU,ZW

The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on
02 September 1999 (02.09.99) under No. WO 99/43427

REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, a **demand for international preliminary examination** must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))

If the applicant wishes to proceed with the international application in the **national phase**, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Authorized officer

J. Zahra

Facsimile No. (41-22) 740.14.35

Telephone No. (41-22) 338.83.38

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU 10 -10- 1999

PCT

INFORMATION CONCERNING ELECTED OFFICES NOTIFIED OF THEIR ELECTION

(PCT Rule 61.3)

To:

HESS, Yitzhak
Dr. Yitzhak Hess & Partners
P.O. Box 6451
61063 Tel Aviv
ISRAËL

Date of mailing (day/month/year)

23 September 1999 (23.09.99)

Applicant's or agent's file reference

8244

IMPORTANT INFORMATION

International application No.

PCT/IL99/00097

International filing date (day/month/year)

16 February 1999 (16.02.99)

Priority date (day/month/year)

26 February 1998 (26.02.98)

Applicant

YISSUM RESEARCH DEVELOPMENT COMPANY OF THE HEBREW UNIVERSITY OF JERUSALEM
et al

1. The applicant is hereby informed that the International Bureau has, according to Article 31(7), notified each of the following Offices of its election:

AP : GH, GM, KE, LS, MW, SD, SZ, UG, ZW

EP : AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE

National : AU, BG, BR, CA, CN, CZ, DE, GB, IL, JP, KP, KR, MN, NO, NZ, PL, RO, RU, SE, SK, US

2. The following Offices have waived the requirement for the notification of their election; the notification will be sent to them by the International Bureau only upon their request:

EA : AM, AZ, BY, KG, KZ, MD, RU, TJ, TM

OA : BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG

National : AL, AM, AT, AZ, BA, BB, BY, CH, CU, DK, EE, ES, FI, GD, GE, GH, GM, HR, HU, ID, IN, IS, KE, KG, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MW, MX, PT, SD, SG, SI, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW

3. The applicant is reminded that he must enter the "national phase" before the expiration of 30 months from the priority date before each of the Offices listed above. This must be done by paying the national fee(s) and furnishing, if prescribed, a translation of the international application (Article 39(1)(a)), as well as, where applicable, by furnishing a translation of any annexes of the international preliminary examination report (Article 36(3)(b) and Rule 74.1).

Some offices have fixed time limits expiring later than the above-mentioned time limit. For detailed information about the applicable time limits and the acts to be performed upon entry into the national phase before a particular Office, see Volume II of the PCT Applicant's Guide.

The entry into the European regional phase is postponed until 31 months from the priority date for all States designated for the purposes of obtaining a European patent.

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. (41-22) 740.14.35

Authorized officer:

C. Carrié

C. Carrié

Telephone No. (41-22) 338.83.38

PATENT COOPERATION TREATY

From the:
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

Yitzhak, Hess & Partners
P.O.Box 6451
TEL-AVIV 61063
ISRAEL

PCT

WRITTEN OPINION

(PCT Rule 66)

Date of mailing
(day/month/year)

19. 10. 99

Applicant's or agent's file reference

8244

REPLY DUE

within 3 month(s)

from the above date of mailing

International application No.

PCT/IL99/00097

International filing date (day/month/year)

16/02/1999

Priority date (day/month/year)

26/02/1998

International Patent Classification (IPC) or both national classification and IPC

B01J13/02

Applicant

YISSUM RESEARCH DEVELOPMENT COMPANY OF THE..et al.

1. This written opinion is the **first** drawn up by this International Preliminary Examining Authority.

2. This opinion contains indications relating to the following items:

- I ☒ Basis of the opinion
- II ☐ Priority
- III ☒ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain document cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

3. The applicant is hereby **invited to reply** to this opinion.

When? See the time limit indicated above. The applicant may, before the expiration of that time limit, request this Authority to grant an extension, see Rule 66.2(d).

How? By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. For the form and the language of the amendments, see Rules 66.8 and 66.9.

Also: For an additional opportunity to submit amendments, see Rule 66.4.
For the examiner's obligation to consider amendments and/or arguments, see Rule 66.4 bis.
For an informal communication with the examiner, see Rule 66.6.

If no reply is filed, the international preliminary examination report will be established on the basis of this opinion.

4. The final date by which the international preliminary examination report must be established according to Rule 69.2 is: **26/06/2000**.

Name and mailing address of the international preliminary examining authority:



European Patent Office
D-80298 Munich
Tel. +49 89 2399 - 0 Tx: 523656 epmu d
Fax: +49 89 2399 - 4465

Authorized officer / Examiner

Gosselin, D

Formalities officer (incl. extension of time limits)

Gregoire, J-P

Telephone No. +49 89 2399 8041



I. Basis of the opinion

1. This opinion has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this opinion as "originally filed".*):

Description, pages:

1-7 as originally filed

Claims, No.:

1-11 as originally filed

2. The amendments have resulted in the cancellation of:

☐ the description, pages:

☐ the claims, Nos.:

☐ the drawings, sheets:

3. This opinion has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been and will not be examined in respect of:

☐ the entire international application,

☒ claims Nos. 2,6,

because:

☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (*specify*):

☒ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. 2,6 are so unclear that no meaningful opinion could be formed (*specify*):

see separate sheet

- ☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed.
- ☐ no international search report has been established for the said claims Nos. .

V. Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	1,3-5,7-11
Inventive step (IS)	Claims	1,3-5,7-11
Industrial applicability (IA)	Claims	1,3-5,7-11

2. Citations and explanations

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Re Item V

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Reference is made to the following document:

D1 = WO 97 24 224 A

2. D1 discloses a process for the preparation of nanoparticles of metals. The particles are synthesised from solution of precursors, which are reacted with a reducing agent. The method involves the use of a surfactant. In view of the examples, the reaction conditions can be qualified as mild. The nanoparticles can be additionally dispersed in a polymer solution. The solvent comprises ethers and chlorinated hydrocarbons. The polymers i.a. polymethylmetacrylate. (D1: claims more particularly claims 1, 14, 20, 21, 23 and 24).

Notwithstanding the objections under Article 6 PCT (Re Item VIII) the method according to claims 1, 3 to 5, 7 and 10 of the application lacks novelty in terms of Article 33(1) and (2) PCT over the content of D1.

3. It is not at present apparent which part of the application could serve as a basis for a new, allowable claim. Should the applicant nevertheless regard some particular matter as patentable, the Applicant should file an independent claim including such matter taking account of Rule 6 PCT (two part form).

The applicant should also indicate in the letter accompanying the claims the difference of the subject-matter of the new claim vis-à-vis the state of the art and the significance thereof, i.e. the Applicant should discuss the novelty and the inventive step following the problem/solution approach, or provide evidence that a technical effect, which could not be expected by a skilled man, has been obtained.

The technical problem to be defined should be defined over the disclosure of the closest prior art and further supported by the application documents as originally filed, otherwise it should be considered that the subject-matter of the application has been enlarged beyond the content of the application as originally filed (inventive

realised after the filing date)(Article 34(2)b PCT). The Applicant should indicate the support for the technical problem in the application as originally filed.

The description must be brought into conformity with the new claims to be filed; care should be taken during revision, especially of the introductory portion including any statements of problem or advantage, not to add subject-matter which extends beyond the content of the application as originally filed. The amendments should be done according to Rule 66.8 PCT.

Re Item VIII

Certain observations on the international application

1. The abusive use of non conventional terms and relative terms renders the subject-matter of the claims as a whole obscure.
 - 1a. In common language, a precursor would be the starting material, which after reaction, leads to meta, metal oxide or ceramics nanoparticles. A surfactant does not seem to belong to this type of materials, although according to claim 1, the precursor is a compound selected among surfactants and alkoxides.

Moreover, the content of claim 9 is in contradiction with the precursor definition according to claim 1, because it refers to metal compounds, which are not alkoxides.

- 1b. In the present form, the method of claim 1 is merely defined by reference to the technical problem that the applicant intends to solve. Claim 1 does not meet the requirements of Article 6 PCT in that the matter for which protection is sought is not clearly defined. The technical features "suitable" or necessary for achieving this result should be added.
 - 1c. It is also submitted that there is a discrepancy between the subject-matter of claim 1 and the description, page 4, lines 19-28. According to the description, the feature of claim 2 is an essential feature.

- 1d. Moreover, "non freezing water" is not a definition commonly recognised in the art. Since this term is not concisely defined in the application and the publications cited in the application are not available to the examiner, claims 1 and 2 do also not meet the requirement of clarity and conciseness in view of these terms.

In view of the information contained in the description, non freezing water should correspond to water molecules strongly bond to a surface. In the present case, the compounds to the surface of which the water is bounded is not identified.

- 1e. The terms "organized water-organic surfactants" is not understood. Microemulsions and liquid crystalline media, which are mentioned by way of example, does not necessarily an organic surfactant. In the context of the application, the meaning of "organized" is also obscure.

It further appears that the wording of claim 6 is not consistent with that of the description, page 4, lines 38-40.



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Date

PCT/IL99/00097

8244

January 16th, 2000

BY COURRIER

AND BY FAX: 49 [89] 2399-4465

Mr. D. Gosselin
European Patent Office
Headquarters at Munich
Erhardstr. 27
D-80331 Munich
G E R M A N Y

Dear Sirs,

Re: **Patent Application No. PCT/IL99/00097**
In the name of Yissum Research Development Company of the . . . et al.

In response to the written opinion mailed on October 19th, 1999, we send you herewith the following:

- ♦ Answers to the written opinion
- ♦ New Specification

The answers refer exactly to the points raised by the Examiner and the Specification is drafted in accordance with the explanations given by the Inventor.

Yours very truly,
DR. YITZHAK HESS & PARTNERS


Dr. Yitzhak Hess

Please acknowledge receipt of this letter with enclosures by returning a copy of this letter, which is enclosed herewith.

The answer to referee's remarks

In accordance with referee contention, we provided the following change of the specification "Methods for the preparation of nanosized material particles"

Parts of "field of invention" "background of invention" and "brief statement of invention" are overwritten in order to clarify novelty, inventive step and industrial applicability. The list of references is now organized in the end of text.

Answers on "Certain observations" presented on separate sheet 2.

In regard to 1a.

Special surfactants comprising metal ions, which have to be reduced (for instance, Cu, Cd sulfosuccinate or $[\text{PdCl}_4][\text{R}_4\text{N}]$, where $[\text{R}_4\text{N}]$ is quaternary ammonium cation) may be regarded as surfactants and metal organic salts simultaneously. These compounds are metal precursors. However, we agree that such definition makes Claim (1) ambiguous. Therefore, the new draft considers mentioned compounds in the group of organic metal salts. Correspondingly, claim 1 has been changed, as now is represented in Claim (1) of the new draft.

In Claim 6 (in new draft 5) lines 20-22 are overwritten as:

...wherein the complex liquids are selected among organized water-organic-surfactant solutions (O/W microemulsions and liquid crystalline media).

Claim (9) (in new draft 8) remains unchanged. The content of Claim (9) of original draft is consistent with the precursor definition according to Claim (1) in new draft, since metal alkoxides are precursors for metal oxides (not the metals).

In regard to 1b.

The expression "suitable" in Claim (1) is concretized in subsequent corresponding claims.

We have no objection to consider Claim (2) as an essential feature and thus, we mentioned it in Claim (1). Respectively, the numeration of claims changed as to one number less.

In regard to 1c.

The discrepancy between subject-matter of Claim (1) of the new draft and the description, page 4 , lines 19-28, in the original draft does not exist any more.

In regard to 1d.

In new draft we presented the definition of non freezing water in accordance with that accepted in scientific literature devoted to surfactants in solution behavior. In context of the invention, “bound water” are bound to the hydrophilic parts of the surfactant molecules.

In regard to 1 e.

Term “organized water-organic surfactant” actually is a mistake. In all cases where it appeared in the text we changed it as “organized water-organic-surfactant “.

Claim 6, lines 20-22 are overwritten as:

...wherein the complex liquids are selected among organized water-organic-surfactant solutions (O/W microemulsions and liquid crystalline media).

After that, the wording of Claim (6) (new 5) becomes consistent with that of the description, page 4, lines 38-40 in the original draft.

The difference of present invention from PCT /US 96/20402 concludes in the following.

- The key factor of PCT /US 96/20402 is using functional ligands, which are covalently bound to metal particles (due to formation of metal complexes on the bare metal surface). The key factors of the present invention are the structure of organized water-organic-surfactant solution and non-freezing water.
- The present invention has no restriction to precursor dissolution (organic or water phase) while PCT /US 96/20402 method involves the precursors only soluble in water.
- The present invention utilizes reducing, hydrolysis-condensation and exchange types of reactions and enables to produce metal, metal oxide and ceramic nanoparticles. PCT /US 96/20402 involves only the reduction and produces only metal nanoparticles. The upper limit of nanoparticle dimensions is 5 nm for

present invention and 20 nm for PCT /US 96/20402. Both methods enable to synthesize particles with narrow size distributions.

- The present invention directly produces particle dispersions which may be used in film formulations. Method of PCT /US 96/20402 requires the necessary step of particle isolation.
- In the present invention surfactant aggregates which are present in surfactant-water-organic solutions provide restricted reaction media for inorganic material synthesis. Surfactant molecules are stabilizers for the produced nanosize particles. Method of PCT /US 96/20402 used surfactants for metal crystallites isolation and redispersion, while particle stabilizers are functionalized ligands.

METHODS FOR THE PREPARATION OF NANOSIZED MATERIAL PARTICLES

Field of invention

The present invention relates to the methods for the preparation of low nanometer range inorganic particles. (The nanoparticles in connection with present invention comprise transition metals and alloys; metal oxides and proc ceramic compositions being of a low nanometer range i. e. about 1-5 nm). Nanomaterials are prepared from the corresponding precursors, i.e. transition metal complexes, salts and alkoxides by corresponding chemical reactions, e.g. reduction, hydrolysis-condensation and exchange processes under mild conditions.

Said nanoparticles (after isolation and redispersion or using as prepared) provide fine colloidal dispersions in different solutions which make them suitable for film deposition on various supports.

Background of the invention

The contemporary electronic and some related industries mainly use ion implantation [1] and organometallic chemical vapor deposition [2,3] for preparation thin films, comprising inorganic nanoparticles on solid supports. These expensive methods enable to provide films with high physical-mechanical properties, but they have poor possibility to control particle size distribution. The main parameters which determine electronic and physical-chemical properties of materials being in nanometer range, are particle dimension and degree of polydispersity. For some applications, electronic, optical and catalytic materials have to comprise particles of low nanometer range which possess of narrow size distributions. The iWetf method, which is a method of

film deposition from solutions, provides a good challenge for the industry since it does not require high temperatures and pressures or the high vacuum, while it enables to control particle dispersity and thus, to vary the properties of nanocomposites to a large extent.

During the last decade, the number of scientific works devoted to the synthesis of nanometer range materials in liquid media has significantly increased. Certain practical results were reported. Thus, for example Schmid [4] demonstrated that the pellets which consist of ligand stabilized golden clusters (prepared in liquid) may be regarded as tunneling resonance resistors and, additionally, as cellular automates. Electrically conducting polymers were successfully prepared by implement of organosols of metal sulfides [5]. The polymer-composite films not only show a good electrical conductivity but were also controlled to p - or n - type conductors. Hybrid organic-inorganic films were successfully used as optical transparent scratch resistant coatings on glass and plastics [6].

Synthesis of nanosized metal and alloys, metal oxides and sulfides was provided in mono- and two-phase liquid systems containing particle stabilizers (specific complexing ligands and surfactant molecules [1, 7-12]. The direction of particle synthesis in the surface films also is developing [13,14]. Some of these methods lead to preparation of nanoparticles with rather narrow size distributions, but the prepared particles difficulty isolate and redisperse with aggregation, which make them not suitable for preparation of formulations useful for coatings. The only methods which produce redispersible particles are those, which imply reductive synthesis and quaternary ammonium derivatives, served as phase transfer agents or/and particle stabilizers. Nanometer-scale metal crystallites functionalized by organic ligands, prepared in two-phase solutions by phase transfer process were useful for preparation

of composite coating formulations [15]. Although, this method gives rise to regulate particle size and stability it has the important restrictions which are: a) only metal ion compounds soluble in water may be used as metal precursor; b) functional ligands have to be covalently bound to metal particles that necessary assume the specific metal-ligand interaction.

Brief statement of the invention

The present invention propose the preparation of particles in complex liquids which are organized water-organic-surfactant solutions (microemulsions, liquid crystals). Said solutions are thermodynamically stable systems and show spatial microheterogeneity with 1-40 nm monodisperse oil and water domains [16]. Factors regulating the structure formation and growth of inorganic phases arise from the possibility of providing spatially restricted inorganic material synthesis by confining the reaction solutions within organized media of organic amphiphiles. Reaction in such systems work with the concept that growth processes are limited in nanostructured matrices (microemulsions, liquid crystals) by the size of structures themselves. The confined synthesis of inorganic phases provided in organized water-organic surfactant solutions leads to producing nonaggregated particles, which have to be in thermodynamic equilibrium with one another and with the surfactant aggregates. This occurred if particle size is like the surfactant intraaggregate space size.

The state of water in organized water-organic-surfactant solutions is indicative of the surfactant intraaggregate space (dimension of aggregates in the reversed microemulsions or liquid crystals increases with water[16]). Only small quantity of water molecules may be bound to the surfactant hydrophilic part (up to 3 water molecular layers closest to aggregate interface [17]), the rest water molecules in

water domains organize in bulk water. The bound water thermodynamic properties are sufficiently modified while bulk or free water has physical-chemical properties which are not very different from those of pure water. According to the method utilized by Senatra [18], in which endothermic scaling mode was applied, it was accepted that free water melts at 0°C , interfacial bound water melts at -10°C , and non freezing water, which is the most strongly part of bound water, has no peaks on thermograms extend to -100°C . Therefore, the lack of water melting events on sub-zero DSC (differential scanning calorimetry) thermograms, which is indicative of nonfreezing water in the system, signs the smallest surfactant intraggregate space. Accordingly, inorganic particles synthesized in such systems, possess of small (1-5 nm) size, narrow size distributions, and shape which resembles the shape of surfactant aggregates.

To prepare small nanometer range nanoparticles one might avoid the inorganic particle uncontrolled growth. In this regard, the lack of free or weakly bound water in the surfactant aggregates lowers their attraction and hinder the inorganic particle growth. In special case of hydrolysis-condensation reactions of metal and silicon alkoxides, involving strongly bound (non freezing) water molecules in the reaction in turn, facilitates producing the small particles due to the control of reaction kinetics.

Therefore, the state of water in organized water-organic-surfactant solutions (strongly bound, non freezing) is a key factor which governs the desired small size of synthesized inorganic particles from molecular precursors.

The methods implied in the present invention are suitable for wide range of inorganic phase precursors soluble in different polar or apolar solvents, it does not assume the specific interactions with stabilizing molecules and gives rise to control particle dimension in low nanometer range (1-5 nm), with narrow size distributions. Many

types of reactions - reduction, hydrolysis, exchange-, may be involved. Such produced inorganic particles evidence fine colloidal structures in the matrices solutions which are able to use as coatings. Said colloidal structures are compatible with supplementary liquid components of coating formulations. And, finally, they may be isolated and redispersed without aggregation in number of solvents, which broadens the spectrum of their application in different coating formulations (for instance, for coating of conventional powders)

In developing the method according to the present invention it has been considered:

- i) producing the water-organic-surfactant organized solutions (complex liquids) comprising nanosized particles in particular having a diameter of 1 - 5 nm which are useful for the coating preparation;
- ii) regulating the water content in such a manner that the whole water will be non-freezing (strongly bound to the surfactant), thus enabling to provide nanoparticles which have a diameter of less than 5 nm;
- iii) the regulation of the solution structures which enable the regulation of the morphology of the particles;
- iv) the variation of the chemical composition and concentration of nano-precursors (and of the complementary reactants), which enables to control of the particle size distributions (PSD) and of the thickness of the particle protection shells;
- v) using different polymers which enable the production of films having different adhesion properties, by the deep coating method; and
- vi) the control of the solutions viscosity and the velocity of withdrawing which lead to different film thicknesses.

The optimization of the above mentioned factors (which should operate simultaneously) should lead to the production of the coatings having the desired properties.

The present invention thus consists in a method for the production of nanomaterial particles (as herein defined) in which:

said nanomaterial particles are synthesized in complex liquids containing non-freezing water from suitable precursors, which precursors are selected from metal complexes, salts and alkoxides by a suitable chemical reactions under mild conditions; and

preparing from said materials fine colloids dispersed in various polymer solutions.

The nanomaterial particles have advantageously a dimension of 1 - 5 nm.

The water in the solution is advantageously non - freezing water (as determined by low temperature differential scanning calorimetry).

The suitable chemical reaction may be selected, for example, among reduction, hydrolysis and exchange processes.

Mild condition with connection in present invention are suitable atmospheric pressure and temperature range of room temperature to 70°C.

Suitable solutions may be selected among suitable organized water-organic-surfactant solutions; (W/O microemulsions, liquid crystalline media);

Suitable organic solvents may be, e. g selected among suitable hydrocarbons (octane, decane, dodecane); chlorinated hydrocarbons (1,2 - dichloroethane); ethers (ethylether); etc.

The appropriate liquid media enables the preparation of different self-assemblies of nanomaterials and subsequently the use of them as thin films on various supports.

Suitable surfactants are, for example,:

Quaternary ammonium salts, e.g. trioctylmethylammonium chloride (aliquat 336); dioctyldimethylammonium bromide (DDAB); cetyltrimethylammonium chloride (CTAB); sodium bis (2-ethylhexyl) - sulfosuccinate; and poly ethoxyethylene - 10-oleyl ether (Brij 96); etc.

Silicon and metal oxides precursors may be, e.g. alkoxides:

alkoxysilanes (tetramethoxysilane TMOS, tetraethoxysilane TEOS); Al, Zr isopropoxides;

Fe, Mg and Al chlorides; Al and Mg acetates, Na and K orthosilicates, Zr oxychloride etc.

Metal precursors may be e. g.

transition metal salts of Fe, Co, Ni, Cu, Ru, Rh, Pd, Ir and Pt, e.g. K_2PdCl_4 , K_2PtCl_6 , $CuCl_2$, $[PdCl_4][R_4N]^+$, Cu sulfosuccinate, etc.

The polymers may be selected, e.g. from polyethylene oxide (PEO); polyvinyl chloride (PVC), polyvinyl alcohol (PVA); polymethyl methacrylate (PMMA), etc.

Suitable reducing agents are, for example, sodium formate, hydrogen and certain alcohols (methanol, ethanol, isopropylalcohol), etc.

The method according to the present invention can direct the morphology, dimension and homogeneity of the dimension and homogeneity of the sized distributions of the small colloids (and clusters) and also their self-assembling.

Claims

1. A method for the production of nanomaterial particles (as herein defined) in which:

said nanomaterial particles are synthesized in complex liquids, where the whole water is non freezing water, from immobilized precursors, which precursors are selected from metal complexes, metal salts and alkoxides, by a particular chemical reaction;

and preparing from said materials fine colloids dispersed in various polymer solutions.
2. A method according to Claim 1 wherein the nanomaterial particles have a dimension of 1-5 nm.
3. A method according to any of Claims 1 to 2 , wherein the mild conditions are atmospheric pressure and a temperature range of room temperature to 70°C.
4. A method according to any of Claims 1 to 3, wherein the chemical reaction is selected among a hydrolysis, reduction and exchange processes.
5. A method according to any of Claims 1 to 4, wherein the systems are selected among organized water-organic-surfactant solutions (O/W microemulsions and liquid crystalline media).
6. A method according to any of Claims 1 to 5, wherein the solvent is selected among suitable hydrocarbons (octane, decane, dodecane), chlorinated hydrocarbons (1-2 dichloroethane); and ethers (ethylether).
7. A method according to any of Claims 1 to 5, wherein the surfactants are selected among trioctylmethylammonium chloride (aliquat 336); dioctyldimethylammonium bromide (DDAB); cetyltrimethylammonium chloride

(CTAB); sodium bis (2-ethylhexyl) - sulfosuccinate; and poly- ethoxyethylene - 10-oleyl ether.

8. A method according to any of Claims 1 to 5, wherein oxides and metal precursors are selected among alkoxysilanes (tetramethoxysilane TMOS, tetraethoxysilane TEOS); Al, Zr isopropoxides; Fe, Mg and Al chlorides; Al and Mg acetates, Na and K orthosilicates, Zr oxychloride and transition metal complex salts of Fe, Co, Ni, Cu, Ru, Rh, Pd, Ir and Pt.
9. A method according to any of Claims 1 to 8, wherein the polymers are selected among polyethylene oxide (PEO); polyvinyl chloride (PVC), polyvinyl alcohol (PVA); and polymethyl methacrylate (PMMA).
10. A method according to any of Claims 4 to 9, wherein the reducing agent is selected among sodium formate, hydrogen and certain alcohols (methanol, ethanol, isopropylalcohol).

References

1. Che, M.; Bennet, C.,O.; *Advanced Catal.*, **36** (1989) 55.
2. Sherman, A.; *Chemical Vapor Deposition for Microelectronics, Principals, Technology and Application*, Park Ridge, New-York (1987).
3. Poppa, H.; *Catal. Rev - Sci. Eng.*, **35(3)** (1993) 359.
4. Schmid, G.; *Chem. Review*, **92** (1992) 1709.
5. Yamamoto, T; in *Macromolecular Complexes, Dynamic Interactions and Electronic Processes*, (Eishum Tsuchida Ed.), VCH (1993) 380.
6. Schmidt, H.; Kasemann, R.; Burkhart, T.; Wagner, G.; Arpac, E.; Geiter, E.; in *Hybrid Organo-Inorgano Composites*, (J Mackenzie Ed.), American Chemical Society, New York (1995) 332.
7. Duff, D., G.; Baker, A.; *Langmuir*, **9** (1993) 2310.
8. Larpent, V.; Le Menn, B; Patin, H.; *New J. Chem.*, **15** (1991) 361.
9. Liz-Marzan, L., M.; Lado-Tourino, I.; *Langmuir*, **12** (1996) 3585.
10. Esumi, K.; Shiratori, M.; Ishizuka, H.; Tano, T; Torigoe, K; Meguro, K.; *Langmuir*, **7** (1991) 457.
11. Bonnemann, H; Brijioux, R.; Brinkmann, R.; Fretzen, R.; Joussen, T.; Koppler, B.; Neiteler, P.; Richter, J.; *J. Mol. Catal.*, **86** (1994) 129.
12. Leff, V.; Ohara, P. C.; Heath, J. R; Gelbart. W. M.; *J. Phys. Chem.*, **99** (1995) 7036.
13. Meguro, K.; Torisuka, N.; Esumi, K.; *Bull. Chem. Soc. Jpn.*, **61** (1988) 341.
14. Meldrum, F., C.; Kotov, N., A.; Fendler, J., H.; *Chem.Mater.*, **7** (1995) 1112.
15. Leff, V.; Heath, H. ; PCT /US96/20402.

16. Kabalnov, A.; Lindman, B.; Olsson, U.; Piquell, L.; Thuresson K.; Wennerstrom, H.; *Coll. Polym. Sci.*, **308** (1996), 274
17. Garti, N., Aserin, A.; Tiunova, I.; Ezrahi, S.; *J. Therm. Anal.*, **51** (1998) 63.
18. Senatra, D.; Carbrielly, G.; Gaminati, G.; Guarini, G.; in *Surfactants in Solution* (K. L. Mittal, Ed.), vol. 10, Plenum Press, New York, (1989) 147.

15-02-2000

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INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

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WRITTEN OPINION

(PCT Rule 66)

Date of mailing
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02.02.00

Applicant's or agent's file reference
8244

REPLY DUE **within 1 month(s)**
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International application No.
PCT/IL99/00097

International filing date (day/month/year)
16/02/1999

Priority date (day/month/year)
26/02/1998

International Patent Classification (IPC) or both national classification and IPC
B01J13/02

Applicant

YISSUM RESEARCH DEVELOPMENT COMPANY OF THE..et al.

1. This written opinion is the **second** drawn up by this International Preliminary Examining Authority.

2. This opinion contains indications relating to the following items:

- I ☒ Basis of the opinion
- II ☐ Priority
- III ☒ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☐ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain document cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

3. The applicant is hereby **invited to reply** to this opinion.

When? See the time limit indicated above. The applicant may, before the expiration of that time limit, request this Authority to grant an extension, see Rule 66.2(d).

How? By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. For the form and the language of the amendments, see Rules 66.8 and 66.9.

Also: For an additional opportunity to submit amendments, see Rule 66.4.
For the examiner's obligation to consider amendments and/or arguments, see Rule 66.4 bis.
For an informal communication with the examiner, see Rule 66.6.

If no reply is filed, the international preliminary examination report will be established on the basis of this opinion.

4. The final date by which the international preliminary examination report must be established according to Rule 69.2 is: 26/06/2000.

Name and mailing address of the international preliminary examining authority:



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Authorized officer / Examiner

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Formalities officer (incl. extension of time limits)
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I. Basis of the opinion

1. This opinion has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this opinion as "originally filed".*):

Description, pages:

1-7 as received on 16/01/2000 with letter of 16/01/2000

Claims, No.:

1-10 as received on 16/01/2000 with letter of 16/01/2000

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. This opinion has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been and will not be examined in respect of:

- ☒ the entire international application,
☐ claims Nos. ,

because:

- ☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (*specify*):
☒ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. 1-10 are so unclear that no meaningful opinion could be formed (*specify*):

s e separate sheet

- ☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed.
- ☐ no international search report has been established for the said claims Nos. .

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

The text of the description and the claims have been completely revised without identifying the nature of the amendments by reference to the application documents as originally filed. Under these conditions it is not possible to properly check whether the amendments meet the requirements of Article 34.2)b) and Rule 66.8 PCT (Cf. also Guidelines PCT/GL/3/VI-7.2, VI-7.3, VI-7.7, VI-7.8, VI-4.12 and VI-4.13).

Moreover, it is also to be considered that the applicant introduced in claim 1 as amended the subject-matter of claim 2 as originally filed. It is still consider that "non-freezing water" is not a definition commonly recognised in the art (communication dated 19.10.99). Consequently, no opinion will be formed with regard to the amended claims as long as the technical feature which is behind the terms "non freezing water" will not have been clarified. The article of Senatra (ref.18) could be filed together with comments showing how it is possible to prepare a complex liquids, where the whole water is non freezing water and how the form of this water in the liquid. It is doubtful that a metastable state in which "non freezing water" could be present can be maintained during the method of production of nanoparticles, which necessarily involves shearing action in the dipersion.

The term "organized water-organic-surfactant" is still not understood. The structure of such a compound and the nature of the bound with metal particles is not understood.

If all the amendments are not clearly and rapidly identified, the International Preliminary Examination Report will be established in view of the application documents as originally filed.

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LIST OF DOCUMENTS FILED WITH THE ISRAEL
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Applicant's or agent's file reference

8244

International application No. (if known)	International filing date (day/month/year) (if known)	(Earliest) Priority date (day/month/year) 26/2/98
Applicant YISSUM RESEARCH DEVELOPMENT COMPANY OF THE HEBREW UNIVERSITY OF JERUSALEM		
Title of the invention METHODS FOR THE PREPARATION OF NANOSIZED MATERIAL PARTICLES		

The applicant hereby requests the RO/IL to acknowledge to the following person (include full name, address, facsimile No. and telephone No.):

DR. YITZHAK HESS & PARTNERS and/or DR. HESS YITZHAK and/or
 HESS-MILUTIN CILA
 P.O.B. 6451 TEL-AVIV 61063, ISRAEL

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| <input type="checkbox"/> | drawings (pages) | |
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POWER OF ATTORNEY

(for an international application filed under the Patent Cooperation Treaty)

(PCT Rule 90.4)

The undersigned applicant(s) (Names should be indicated as they appear in the request):

YISSUM RESEARCH DEVELOPMENT COMPANY OF THE HEBREW
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ISRAEL

hereby appoints (appoint) the following person as:

☒ agent

☐ common representative

Name and address

(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

DR. YITZHAK HESS & PARTNERS and/or
DR. HESS YITZHAK and/or HESS-MILUTIN CILA
P.O.B. 6451 TEL-AVIV 61063, ISRAEL

to represent the undersigned before

☒ all the competent International Authorities

☐ the International Searching Authority only

☐ the International Preliminary Examining Authority only

in connection with the international application identified below:


Title of the invention: METHODS FOR THE PREPARATION OF NANOSIZED MATERIAL
PARTICLES

Applicant's or agent's file reference: 8244

International application number (if already available):

filed with the following Office ISRAEL PATENT OFFICE as receiving Office
and to make or receive payments on behalf of the undersigned.

Signature of the applicant(s) (where there are several applicants, each of them must sign; next to each signature, indicate the name of the person signing and the capacity in which the person signs, if such capacity is not obvious from reading the request or this power):

 MOADENAI PERLMUTTER
MANAGING DIRECTOR & CEO
DECEMBER 24, 1998

Date:

Yissum Research Development Co.
of the Hebrew University of Jerusalem
P.O.B. 4279, Jerusalem, 91042, ISRAEL

PCT

POWER OF ATTORNEY

(for an international application filed under the Patent Cooperation Treaty)

(PCT Rule 90.4)

The undersigned applicant(s) (Names should be indicated as they appear in the request):

GARTI NISSIM
9 Derech Hachochesh St.
Ramot, Jerusalem
Israel

hereby appoints (appoint) the following person as:

☒ agent

☐ common representative

Name and address

(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

DR. YITZHAK HESS & PARTNERS and/or
DR. HESS YITZHAK and/or HESS-MILUTIN CILA
P.O.B. 6451 TEL-AVIV 61063, ISRAEL

to represent the undersigned before

☒ all the competent International Authorities

☐ the International Searching Authority only

☐ the International Preliminary Examining Authority only

in connection with the international application identified below:

Title of the invention: METHODS FOR THE PREPARATION OF NANOSIZED MATERIAL PARTICLES

Applicant's or agent's file reference: 8244

International application number (if already available):

filed with the following Office ISRAEL PATENT OFFICE

and to make or receive payments on behalf of the undersigned.

as receiving Office

Signature of the applicant(s) (where there are several applicants, each of them must sign; next to each signature, indicate the name of the person signing and the capacity in which the person signs, if such capacity is not obvious from reading the request or this power);

Date: 28.12.90 NISS — Garti

POWER OF ATTORNEY

(PCT Rule 90.4)

Date:

25 01.99

[Signature]

PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

International Application No.

International Filing Date

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference
(if desired) (12 characters maximum)

Box No. I TITLE OF INVENTION

METHODS FOR THE PREPARATION OF NANOSIZED MATERIAL PARTICLES

Box No. II APPLICANT

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

YISSUM RESEARCH DEVELOPMENT COMPANY OF THE HEBREW
UNIVERSITY OF JERUSALEM
P.O.B. 4279
Jerusalem 91042, Israel

☐ This person is also inventor.

Telephone No.

Facsimile No.

Teleprinter No.

State (that is, country) of nationality:

ISRAEL

State (that is, country) of residence:

ISRAEL

This person is applicant
for the purposes of:☐ all designated
States☒ all designated States except
the United States of America☐ the United States
of America only☐ the States indicated in
the Supplemental Box

Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

GARTI NISSIM
9 Derech Hachoresh St.
Ramot, Jerusalem
Israel

This person is:

☐ applicant only☒ applicant and inventor☐ inventor only (If this check-box
is marked, do not fill in below.)

State (that is, country) of nationality:

ISRAEL

State (that is, country) of residence:

ISRAEL

This person is applicant
for the purposes of:☐ all designated
States☐ all designated States except
the United States of America☒ the United States
of America only☐ the States indicated in
the Supplemental Box☐ Further applicants and/or (further) inventors are indicated on a continuation sheet.

Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The person identified below is hereby/has been appointed to act on behalf
of the applicant(s) before the competent International Authorities as:☒ agent☐ common representativeName and address: (Family name followed by given name; for a legal entity, full official
designation. The address must include postal code and name of country.)

DR. YITZHAK HESS & PARTNERS and/or DR. HESS YITZHAK
and/or HESS-MILUTIN CILA
P.O.B. 6451 TEL-AVIV 61063, ISRAEL

Telephone No.

03-6042715

Facsimile No.

03-5468038

Teleprinter No.

☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

Continuation of Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

If none of the following sub-boxes is used, this sheet should not be included in the request.

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

BERKOVICH YANA
309/20 HaAnafa St.
Jerusalem 93902
Israel

This person is:

- ☐ applicant only
☒ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

ISRAEL

State (that is, country) of residence:

ISRAEL

This person is applicant for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only
☐ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only
☐ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only
☐ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

☐ Further applicants and/or (further) inventors are indicated on another continuation sheet.

Box No.V	DESIGNATION OF STATES
The following designations are hereby made under Rule 4.9(a) (mark the applicable check-boxes; at least one must be marked):	
Regional Patent	
<input checked="" type="checkbox"/> AR	ARIPO Patent: GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, SD Sudan, SZ Swaziland, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
<input checked="" type="checkbox"/> EA	Eurasian Patent: AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
<input checked="" type="checkbox"/> EP	European Patent: AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT
<input checked="" type="checkbox"/> OA	OAPI Patent: BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line)
National Patent (if other kind of protection or treatment desired, specify on dotted line):	
<input checked="" type="checkbox"/> AL	Albania
<input checked="" type="checkbox"/> AM	Armenia
<input checked="" type="checkbox"/> AT	Austria
<input checked="" type="checkbox"/> AU	Australia
<input checked="" type="checkbox"/> AZ	Azerbaijan
<input checked="" type="checkbox"/> BA	Bosnia and Herzegovina
<input checked="" type="checkbox"/> BB	Barbados
<input checked="" type="checkbox"/> BG	Bulgaria
<input checked="" type="checkbox"/> BR	Brazil
<input checked="" type="checkbox"/> BY	Belarus
<input checked="" type="checkbox"/> CA	Canada
<input checked="" type="checkbox"/> CH and LI	Switzerland and Liechtenstein
<input checked="" type="checkbox"/> CN	China
<input checked="" type="checkbox"/> CU	Cuba
<input checked="" type="checkbox"/> CZ	Czech Republic
<input checked="" type="checkbox"/> DE	Germany
<input checked="" type="checkbox"/> DK	Denmark
<input checked="" type="checkbox"/> EE	Estonia
<input checked="" type="checkbox"/> ES	Spain
<input checked="" type="checkbox"/> FI	Finland
<input checked="" type="checkbox"/> GB	United Kingdom
<input checked="" type="checkbox"/> GD	Grenada
<input checked="" type="checkbox"/> GE	Georgia
<input checked="" type="checkbox"/> GH	Ghana
<input checked="" type="checkbox"/> GM	Gambia
<input checked="" type="checkbox"/> HR	Croatia
<input checked="" type="checkbox"/> HU	Hungary
<input checked="" type="checkbox"/> ID	Indonesia
<input checked="" type="checkbox"/> IL	Israel
<input checked="" type="checkbox"/> IN	India
<input checked="" type="checkbox"/> IS	Iceland
<input checked="" type="checkbox"/> JP	Japan
<input checked="" type="checkbox"/> KE	Kenya
<input checked="" type="checkbox"/> KG	Kyrgyzstan
<input checked="" type="checkbox"/> KP	Democratic People's Republic of Korea
<input checked="" type="checkbox"/> KR	Republic of Korea
<input checked="" type="checkbox"/> KZ	Kazakhstan
<input checked="" type="checkbox"/> LC	Saint Lucia
<input checked="" type="checkbox"/> LK	Sri Lanka
<input checked="" type="checkbox"/> LR	Liberia
<input checked="" type="checkbox"/> LS	Lesotho
<input checked="" type="checkbox"/> LT	Lithuania
<input checked="" type="checkbox"/> LU	Luxembourg
<input checked="" type="checkbox"/> LV	Latvia
<input checked="" type="checkbox"/> MD	Republic of Moldova
<input checked="" type="checkbox"/> MG	Madagascar
<input checked="" type="checkbox"/> MK	The former Yugoslav Republic of Macedonia
<input checked="" type="checkbox"/> MN	Mongolia
<input checked="" type="checkbox"/> MW	Malawi
<input checked="" type="checkbox"/> MX	Mexico
<input checked="" type="checkbox"/> NO	Norway
<input checked="" type="checkbox"/> NZ	New Zealand
<input checked="" type="checkbox"/> PL	Poland
<input checked="" type="checkbox"/> PT	Portugal
<input checked="" type="checkbox"/> RO	Romania
<input checked="" type="checkbox"/> RU	Russian Federation
<input checked="" type="checkbox"/> SD	Sudan
<input checked="" type="checkbox"/> SE	Sweden
<input checked="" type="checkbox"/> SG	Singapore
<input checked="" type="checkbox"/> SI	Slovenia
<input checked="" type="checkbox"/> SK	Slovakia
<input checked="" type="checkbox"/> SL	Sierra Leone
<input checked="" type="checkbox"/> TJ	Tajikistan
<input checked="" type="checkbox"/> TM	Turkmenistan
<input checked="" type="checkbox"/> TR	Turkey
<input checked="" type="checkbox"/> TT	Trinidad and Tobago
<input checked="" type="checkbox"/> UA	Ukraine
<input checked="" type="checkbox"/> UG	Uganda
<input checked="" type="checkbox"/> US	United States of America
<input checked="" type="checkbox"/> UZ	Uzbekistan
<input checked="" type="checkbox"/> VN	Viet Nam
<input checked="" type="checkbox"/> YU	Yugoslavia
<input checked="" type="checkbox"/> ZW	Zimbabwe
Check-boxes reserved for designating States (for the purposes of a national patent) which have become party to the PCT after issuance of this sheet:	
<input type="checkbox"/>
<input type="checkbox"/>
<input type="checkbox"/>
Precautionary Designation Statement: In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation of a designation consists of the filing of a notice specifying that designation and the payment of the designation and confirmation fees. Confirmation must reach the receiving Office within the 15-month time limit.)	

Box No. VI PRIORITY CLAIM☐ Further priority claims are indicated in the Supplemental Box.

Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country	regional application:* regional Office	international application: receiving Office
item (1) 26/2/98	123468	ISRAEL		
item (2)				
item (3)				

☒ The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office) identified above as item(s): 1

* Where the earlier application is an ARIPO application, it is mandatory to indicate in the Supplemental Box at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed (Rule 4.10(b)(ii)). See Supplemental Box.

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA)
(if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):

ISA / EP

Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority):

Date (day/month/year)

Number

Country (or regional Office)

Box No. VIII CHECK LIST; LANGUAGE OF FILING

This international application contains the following number of sheets:

request : 4
description (excluding
sequence listing part) : 7
claims : 2
abstract : 1
drawings :
sequence listing part
of description :
Total number of sheets : 14

This international application is accompanied by the item(s) marked below:

1. ☒ fee calculation sheet
2. ☒ separate signed power of attorney x 3
3. ☐ copy of general power of attorney; reference number, if any:
4. ☐ statement explaining lack of signature
5. ☐ priority document(s) identified in Box No. VI as item(s):
6. ☐ translation of international application into (language):
7. ☐ separate indications concerning deposited microorganism or other biological material
8. ☐ nucleotide and/or amino acid sequence listing in computer readable form
9. ☐ other (specify):

Figure of the drawings which should accompany the abstract:

Language of filing of the international application:

Box No. IX SIGNATURE OF APPLICANT OR AGENT

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).

CILA HESS MILUTIN
PARTNER OF DR. YITZHAK HESS & PARTNERS

For receiving Office use only

1. Date of actual receipt of the purported international application:	2. Drawings: <input type="checkbox"/> received: <input type="checkbox"/> not received:
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:	
4. Date of timely receipt of the required corrections under PCT Article 11(2):	
5. International Searching Authority (if two or more are competent): ISA /	6. <input type="checkbox"/> Transmittal of search copy delayed until search fee is paid.

For International Bureau use only

Date of receipt of the record copy by the International Bureau:

PCT

FEE CALCULATION SHEET

Annex to the Request

For receiving Office use only

International application No.

Applicant's or agent's
file reference

8244

Date stamp of the receiving Office

Applicant

YISSUM RESEARCH DEVELOPMENT COMPANY OF THE HEBREW
UNIVERSITY OF JERUSALEM

CALCULATION OF PRESCRIBED FEES

1. TRANSMITTAL FEE

ILS 402

T

2. SEARCH FEE

US\$ 1338

S

International search to be carried out by EP

(If two or more International Searching Authorities are competent in relation to the international application, indicate the name of the Authority which is chosen to carry out the international search.)

3. INTERNATIONAL FEE

Basic Fee

The international application contains _____ sheets.

first 30 sheets

US\$ 455

b1

_____ x _____ = _____

remaining sheets

additional amount

-

b2

Add amounts entered at b1 and b2 and enter total at B

US\$ 455

B

Designation Fees

The international application contains all designations._____ x 105 = _____number of designation fees
payable (maximum 11)

amount of designation fee

US\$ 1155

D

Add amounts entered at B and D and enter total at I

US\$ 1610

I

(Applicants from certain States are entitled to a reduction of 75% of the international fee. Where the applicant is (or all applicants are) so entitled, the total to be entered at I is 25% of the sum of the amounts entered at B and D.)

4. FEE FOR PRIORITY DOCUMENT (if applicable)

P

5. TOTAL FEES PAYABLE

US\$ 2948 ILS 402

Add amounts entered at T, S, I and P, and enter total in the TOTAL box

TOTAL

☐ The designation fees are not paid at this time.

MODE OF PAYMENT

☐ authorization to charge
deposit account (see below)☐ bank draft☐ coupons☒ cheque☐ cash☐ other (specify):☐ postal money order☐ revenue stamps

DEPOSIT ACCOUNT AUTHORIZATION (this mode of payment may not be available at all receiving Offices)

The RO/ _____ ☐ is hereby authorized to charge the total fees indicated above to my deposit account.☐ is hereby authorized to charge any deficiency or credit any overpayment in the total fees indicated above to my deposit account.☐ is hereby authorized to charge the fee for preparation and transmittal of the priority document to the International Bureau of WIPO to my deposit account.

Deposit Account No.

Date (day/month/year)

Signature